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1. REPORT DATE (DD-MM-YYYY) 13-12-2011		2. REPORT TYPE Final			3. DATES COVERED (From - To) April 2005 - May 2012							
4. TITLE AND SUBTITLE (CII) Programmable Triplet Formation and Decay in Metal-Organic Chromophores				5a. CONTRACT NUMBER								
				5b. GRANT NUMBER FA9550-05-1-0276								
				5c. PROGRAM ELEMENT NUMBER								
6. AUTHOR(S) Castellano, Felix N.				5d. PROJECT NUMBER								
				5e. TASK NUMBER								
				5f. WORK UNIT NUMBER								
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Bowling Green State University, Bowling Green, Ohio 43403-0112					8. PERFORMING ORGANIZATION REPORT NUMBER FPR10380032-75-76							
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAF, AFRL AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203-1768					10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR							
					11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRLL-OSR-VA-TR-2012-0962							
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution A - Approved for Public Release												
13. SUPPLEMENTARY NOTES												
14. ABSTRACT This research project focused on 3 primary areas of investigation. The generalized concept of low power photon upconversion has been developed under the auspices of this funding and has led to broad recognition that this technology, based on regenerative photochemical reactions, can be applied in a range of energy-relevant applications for the conversion of low energy sunlight to higher energy photons. A second focus related to developing systematically-variable photophysics in platinum acetylides, excited-state absorption in particular, for potential applications in optical limiting molecules has resulted in the synthesis and characterization of many new classes of chromophores in addition to theory capable of predicting excited state absorption spectra of select molecules. Finally, new classes of Ru(II) and Os(II) dyes have been developed and tested in operational dye-sensitized solar cells and the record efficiency for an Os(II)-based cell has been achieved as a result of AFOSR support.												
15. SUBJECT TERMS Photon Upconversion, Upconverting Polymers, Metal-Organic Chromophores, Molecular Photophysics, Platinum Acetylide Photophysics, Dye Sensitized Solar Cells, Ruthenium(II) Dyes, Osmium(II) Dyes												
16. SECURITY CLASSIFICATION OF: <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%; padding: 2px;">a. REPORT</td> <td style="width: 33%; padding: 2px;">b. ABSTRACT</td> <td style="width: 33%; padding: 2px;">c. THIS PAGE</td> </tr> <tr> <td style="text-align: center; padding: 2px;">U</td> <td style="text-align: center; padding: 2px;">U</td> <td style="text-align: center; padding: 2px;">U</td> </tr> </table>			a. REPORT	b. ABSTRACT	c. THIS PAGE	U	U	U	17. LIMITATION OF ABSTRACT U		18. NUMBER OF PAGES 40	
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AFOSR FINAL PERFORMANCE REPORT

PROJECT TITLE: PROGRAMMABLE TRIPLET FORMATION AND DECAY IN METAL-ORGANIC CHROMOPHORES

Start Date: April 15, 2005

Award Number: FA9550-05-1-0276

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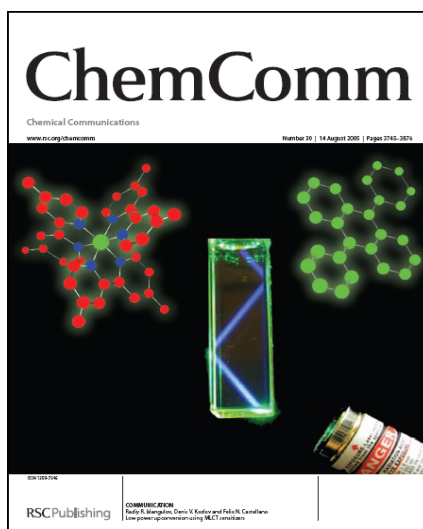
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Summary of Work

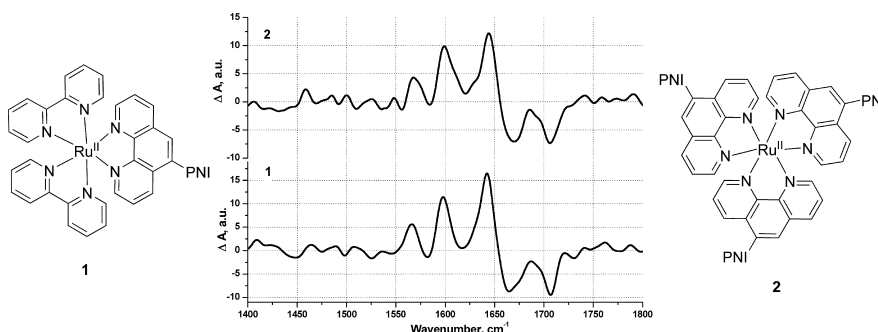
There have been a total of 53 peer-reviewed publications resulting from AFOSR funding under the auspices of the combined awards. In the interest of brevity, executive summaries are provided below for each individual contribution.

Low Power Upconversion Using MLCT Sensitizers. Islangulov, R.R.; Kozlov, D.V.; Castellano, F.N. *Chem. Commun.* **2005**, 3776-3778. (Issue 30 Inside Cover & Featured as Hot Article; C&EN News of the Week Aug. 8, 2005)

Selective low energy excitation of the metal-to-ligand charge transfer (MLCT) transition in $[\text{Ru}(\text{dmb})_3]^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine) in the presence of anthracene or 9,10-diphenylanthracene yields easily visualized upconverted singlet fluorescence resulting from triplet-triplet annihilation at low excitation power.



Observation of Triplet Intraligand Excited States through Nanosecond Step-Scan Fourier Transform Infrared Spectroscopy. Polyansky, D.; Danilov, E. O.; Castellano, F.N. *Inorg. Chem.* **2006**, 45, 2370-2372.



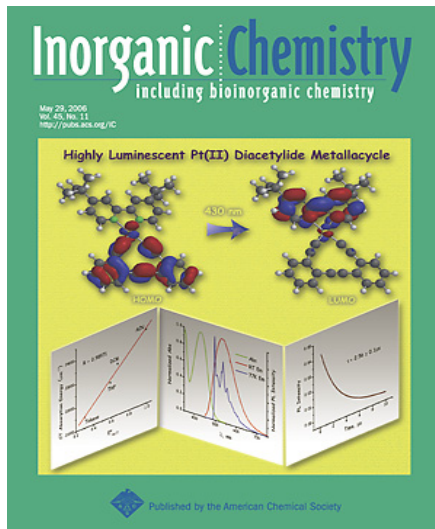
Nanosecond step-scan Fourier transform infrared spectroscopy permits the observation of triplet intraligand (^3IL) character in the excited states of $[\text{Ru}(\text{bpy})_2(\text{PNI-phen})]^{2+}$ and $[\text{Ru}(\text{PNI-phen})_3]^{2+}$ where PNI is 4-piperidinyl-1,8-naphthalimide. After pulsed 355-nm laser excitation, the two ground-state imide

CO bands in each compound are bleached and two substantially lower energy vibrations are produced; the lower energy feature appears as two distinct bands split by an overlapping transient bleach. Model studies confirm that the time-resolved vibrational data are consistent with photoinduced sensitization of the ^3IL excited state. Density functional theory calculations also support these assignments because localization of triplet electron density on the PNI moiety is expected to lead to red-shifted CO vibrations of magnitude similar to those measured experimentally. The current results illustrate that triplet electron density can be directly tracked by time-resolved infrared measurements in metal-organic chromophores and that frequency shifts comparable to those observed in charge-transfer systems can be realized.

Photophysical Processes in Bipyridyl and Terpyridyl Platinum(II) Acetylides. Castellano, F.N.; Pomestchenko, I.E.; Shikhova, E.; Hua, F.; Muro, M.L.; Rajapakse, N. *Coord. Chem. Rev.* **2006**, 250, 1819-1828.

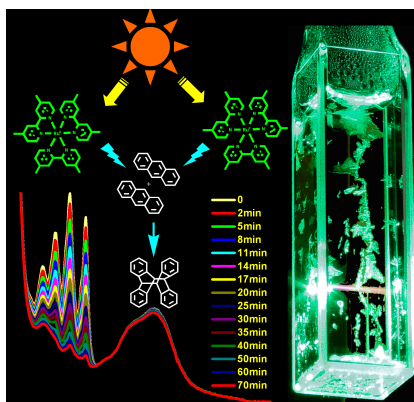
The photophysical properties of mononuclear Pt^{II} chromophores of the general structural formulae: $\text{Pt}(\text{LL})(\text{CCR})_2$ and $[\text{Pt}(\text{LLL})(\text{CCR})]^+$ (LL = substituted or unsubstituted 2,2'-bipyridine; LLL = substituted or unsubstituted 2,2':6',2''-terpyridine; R = aryl or alkyl) are described. Topics related to their preparation, spectroscopy, photochemistry, and photophysics are reviewed.

Platinum(II) Diimine Diacetylides: Metallacyclization Enhances Photophysical Properties. Hua, F.; Kinayyigit, S.; Cable, J.R.; Castellano, F.N. *Inorg. Chem.* **2006**, 45, 4304-4306. *Inorganic Chemistry* Cover May 29, 2006.



The synthesis, structural characterization, and photoluminescence properties of a new platinum(II) diimine complex bearing the bidentate diacetylide ligand tolan-2,2'-diacetylide (tda), $\text{Pt}(\text{dbbpy})(\text{tda})$ [dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine], are described. In CH_2Cl_2 , $\text{Pt}(\text{dbbpy})(\text{tda})$ exhibits a strong visible charge-transfer absorption and broad emission centered at 562 nm. The photoluminescence quantum yield and excited-state lifetime are 0.52 and 2.56 μs , respectively, at room temperature. These parameters indicate that the planarization and rigidity introduced by the cyclic diacetylide leads to a lower-energy-absorbing species displaying enhanced photophysics relative to the analogous $\text{Pt}(\text{dbbpy})(\text{CCPh})_2$. Time-dependent density functional theory calculations, which include solvation by CH_2Cl_2 via the polarizable continuum model, are used to reveal the nature of the excited states in these molecules that are responsible for the charge-transfer transitions. The 77 K emission spectra of the two compounds in EtOH/MeOH glasses are compared, uncovering tda-based ligand-localized phosphorescence in the title compound.

Photochemical Upconversion: Anthracene Dimerization Sensitized to Visible Light using Ru(II) Chromophores. Islangulov, R.R.; Castellano, F.N. *Angew. Chem. Int. Ed.* **2006**, 45, 5957-5959; *Angew. Chem.* **2006**, 118, 6103-6105.

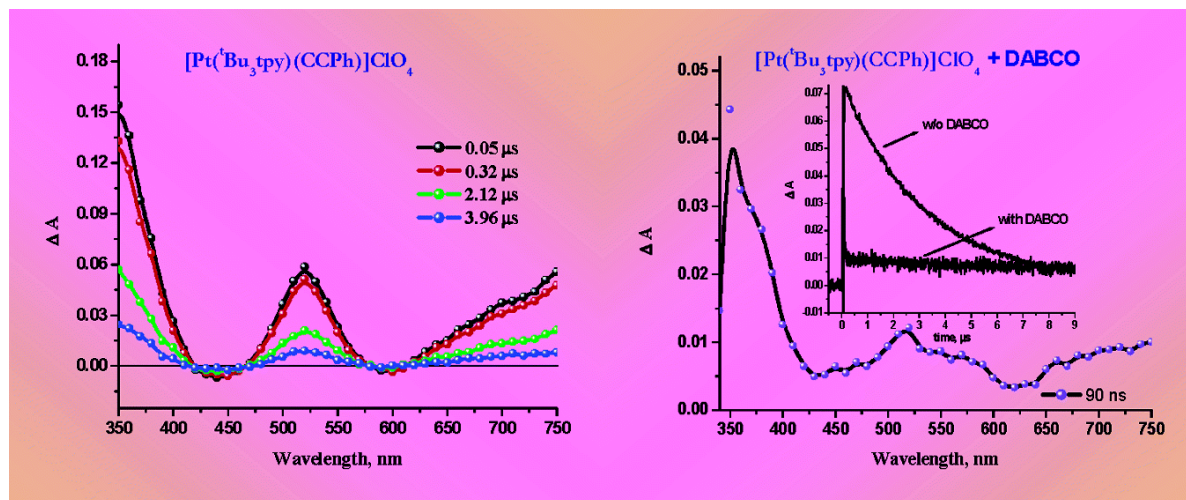


The photodimerization of anthracene serves as a prototype reaction demonstrating the principle of photochemical upconversion utilizing MLCT-sensitized triplet-triplet annihilation. Selective visible excitation of $[\text{Ru}(\text{dmb})_3]^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine) in the presence of anthracene efficiently produces the 4+4 cycloaddition product which traditionally requires the input of ultraviolet light to achieve the same chemical transformation.

Upconverted Emission from Pyrene and Di-tert-butylpyrene using Ir(ppy)₃ as Triplet Sensitizer. Zhao, W.; Castellano, F.N. *J. Phys. Chem. A* **2006**, 110, 11440-11445.

Metal-to-ligand charge-transfer sensitized upconverted fluorescence in noncovalent triplet energy transfer assemblies is investigated using Ir(ppy)₃ as the sensitizer (ppy = 2-phenylpyridine) and pyrene or 3,8-di-*tert*-butylpyrene as the triplet acceptor/annihilator. Upconverted singlet fluorescence from pyrene or 3,8-di-*tert*-butylpyrene resulting from triplet-triplet annihilation (TTA) is observed following selective excitation of Ir(ppy)₃ in deaerated dichloromethane solutions using 450-nm laser pulses. In both systems, the TTA process is confirmed by the near quadratic dependence of the upconverted fluorescence intensity on incident light power, measured by integrating the upconverted delayed fluorescence kinetic traces as a function of incident excitation power. At the relatively high concentrations of pyrene that were utilized, pyrene excimer formation was detected by its characteristic broad emission centered near 470 nm. In essence, selective excitation of Ir(ppy)₃ ultimately resulted in the simultaneous sensitization of both singlet pyrene and pyrene excimers, and the latter degrades the energy stored in the pyrene singlet excited state. Furthermore, in the case of di-*tert*-butylpyrene/Ir(ppy)₃, the formation of excimers is successfully blocked because of the presence of the sterically hindering *tert*-butyl groups. The current work demonstrates that sensitized TTA is indeed accessible to chromophore systems beyond those previously reported, suggesting the generality of the approach.

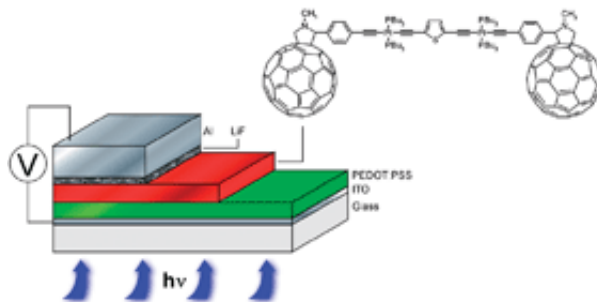
Excited State Absorption Properties of Platinum(II) Terpyridyl Acetylides. Shikhova, E.; Danilov, E.O.; Kinayyigit, S.; Pomestchenko, I.E.; Tregubov, A. D.; Camerel, F.; Retaillieu, P.; Ziessel, R.; Castellano, F.N. *Inorg. Chem.* **2007**, 46, 3038-3048.



A comprehensive photophysical study is presented which compares the ground- and excited-state properties of four platinum(II) terpyridyl acetylide compounds of the general formula $[\text{Pt}(\text{tBu}_3\text{tpy})(\text{C}\equiv\text{CR})]^+$, where tBu_3tpy is 4,4',4'-tri-*tert*-butyl-2,2':6',2'-terpyridine and R is an alkyl or aryl group. $[\text{Ru}(\text{tBu}_3\text{tpy})_3]^{2+}$ and the pivotal synthetic precursor $[\text{Pt}(\text{tBu}_3\text{tpy})\text{Cl}]^+$ were also investigated in the current work. The latter two complexes possess short excited-state lifetimes and were investigated using ultrafast spectrometry while the other four compounds were evaluated using conventional nanosecond transient-absorption spectroscopy. The original intention of this study was to comprehend the nature of the impressive excited-state absorptions that emanate from this class of transition-metal chromophores. Transient-absorbance-difference spectra across the series contain the same salient features, which are modulated only slightly in wavelength and markedly in intensity as a function of the appended acetylide ligand. More intense absorption transients are observed in the arylacetylide structures relative to those bearing an alkylacetylide, consistent with transitions coupled to the π system of the ancillary ligand. Reductive spectroelectrochemical measurements successfully generated the electronic spectrum of the tBu_3tpy radical anion in all six complexes at room temperature. These measurements confirm that electronic absorptions associated with the tBu_3tpy radical anion simply do not account for the intense optical transitions observed in the excited state of the Pt(II) chromophores. Transient-trapping experiments using the spectroscopically silent reductive quencher DABCO clearly demonstrate the loss of most transient-absorption features in the acetylide complexes throughout the UV, visible, and near-IR regions following bimolecular excited-state electron transfer, suggesting that these features are strongly tied to the photogenerated hole which is delocalized across the Pt center and the ancillary acetylide ligand.

A Fulleropyrrolidine End-Capped Platinum-Acetylide Triad: The Mechanism of Photoinduced Charge Transfer in Organometallic Photovoltaic Cells. Guo, F.; Ogawa, K.; Kim, Y.-G.; Danilov, E.O.; Castellano, F.N.; Reynolds, J.R.; Schanze, K.S. *Phys. Chem. Chem. Phys.* **2007**, 9, 2724-2734.

The fullerene end-capped platinum acetylide donor-acceptor triad $\text{Pt}_2\text{ThC}_{60}$ was synthesized and characterized by using photophysical methods and photovoltaic device testing. The triad consists of the platinum acetylide oligomer $\text{Ph-CC-Pt(PBu}_3)_2\text{-CC-Th-CC-Pt(PBu}_3)_2\text{-CC-Ph}$ (Ph = phenyl and Th = 2,5-thienyl, stereochemistry at both Pt centers is *trans*) that contains fulleropyrrolidine moieties on each of the terminal phenylene units. Electrochemistry of the triad reveals relatively low potential oxidation and reduction waves corresponding, respectively, to oxidation of the platinum acetylide and reduction of the fulleropyrrolidine units. Photoluminescence spectroscopy shows that the singlet and triplet states of the platinum acetylide chromophore are strongly quenched in the triad assembly, both in solution at ambient temperature as well as in a low-temperature solvent glass. The excited state quenching arises due to intramolecular photoinduced electron transfer to produce a charge separated state based on charge transfer from the platinum acetylide (donor) to the fulleropyrrolidine (acceptor). Picosecond time resolved absorption spectroscopy confirms that the charge transfer state is produced within 1 ps of photoexcitation, and it decays by charge recombination within 400 ps. Organic photovoltaic devices fabricated using spin-coated films of $\text{Pt}_2\text{ThC}_{60}$ as the active material operate with modest efficiency, exhibiting a short circuit photocurrent of 0.51 mA cm^{-2} and an open circuit voltage of 0.41 V under 100 mW cm^{-2} /AM1.5 illumination. The results are discussed in terms of the relationship between the mechanism of photoinduced electron transfer in the triad and the comparatively efficient photovoltaic response exhibited by the material.



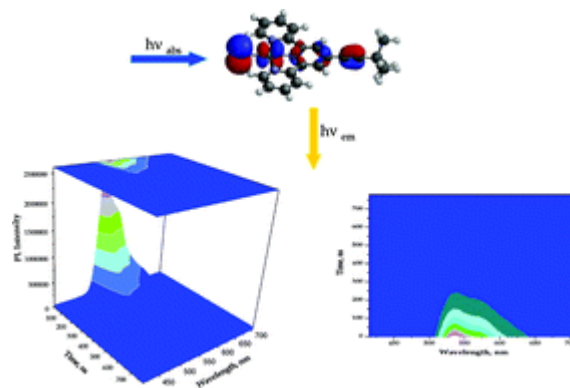
Luminescent Charge Transfer Platinum(II) Metallacycle. Hua, F.; Kinayyigit, S.; Rachford, A.A.; Shikhova, E.A.; Goeb, S.; Adams, C.J. Cable, J.R.; Kirschbaum, K.; Pinkerton, A.A.; Castellano, F.N. *Inorg. Chem.* **2007**, 46, 8771-8783.

The photophysical and electrochemical properties of a platinum(II) diimine complex bearing the bidentate diacetylide ligand tolan-2,2'-diacetylide (tda), $\text{Pt}(\text{dbbpy})(\text{tda})$ [dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine] (1), are compared with two reference compounds, $\text{Pt}(\text{dbbpy})(\text{C}\equiv\text{CPh})_2$ (2) and $\text{Pt}(\text{dppp})\text{tda}$ [dppp = 1,3-bis(diphenylphosphino)propane] (3), respectively. The X-ray crystal structure of 1 is reported, which illustrates the nearly perfect square planarity exhibited by this metallacycle. Chromophore 2 possesses low-lying charge-transfer excited states analogous to 1, whereas structure 3 lacks such excited states but features a low-lying platinum-perturbed tda intraligand triplet manifold. In CH_2Cl_2 , 1 exhibits a broad emission centered at 562 nm at ambient temperature, similar to 2, but with a higher photoluminescence quantum yield and longer excited-state lifetime. In both instances, the photoluminescence is consistent with triplet-charge-transfer excited-state parentage. The rigidity imposed by the cyclic diacetylide ligand in 1 leads to a reduction in nonradiative decay, which enhances its room-temperature photophysical

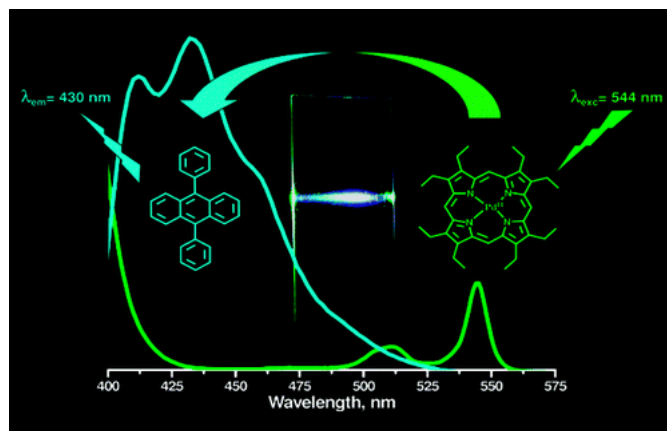
properties. By comparison, 3 radiates highly structured tda-localized triplet-state phosphorescence at room temperature. The 77 K emission spectrum of 1 in 4:1 EtOH/MeOH becomes structured and is quantitatively similar to that measured for 3 under the same conditions. Because the 77 K spectra are nearly identical, the emissions are assigned as (3) tda in nature, implying that the charge-transfer states are raised in energy, relative to the (3) tda levels in 1 in the low-temperature glass. Nanosecond transient absorption spectrometry and ultrafast difference spectra were determined for 1-3 in CH₂Cl₂ and DMF at ambient temperature. In 1 and 2, the major absorption transients are consistent with the one-electron reduced complexes, corroborated by reductive spectroelectrochemical measurements performed at room temperature. As 3 does not possess any charge-transfer character, excitation into the pipi* transitions of the tda ligand generated transient absorptions in the relaxed excited state assigned to the ligand-localized triplet state. In all three cases, the excited-state lifetimes measured by transient absorption are similar to those measured by time-resolved photoluminescence, suggesting that the same excited states giving rise to the photoluminescence are responsible for the absorption transients. ESR spectroscopy of the anions 1- and 2- and reductive spectroelectrochemistry of 1 and 2 revealed a LUMO based largely on the pi* orbital of the dbbpy ligand. Time-dependent density functional theory calculations performed on 1-3 both in vacuum and in a CH₂Cl₂ continuum revealed the molecular orbitals, energies, dipole moments, and oscillator strengths for the various electronic transitions in these molecules. A DeltaSCF-method-derived shift applied to the calculated transition energies in the solvent continuum yielded good agreement between theory and experiment for each molecule in this study.

Room Temperature Luminescence from [Pt(4'-C≡CR-tpy)Cl]⁺ Complexes. Muro, M.L.; Castellano, F.N. *Dalton Trans.* **2007**, 41, 4659 - 4665. (*Dalton Transactions* Cover November 7, 2007 Cover)

The synthesis, photophysics, electronic structure, and electrochemical characterization of 4'-*tert*-butylacetylene-2,2':6',2''-terpyridineplatinum(II) chloride (1), 4'-phenylacetylene-2,2':6',2''-terpyridineplatinum(II) chloride (2), and their Zn^{II} analogs are described. The Pt^{II} complexes display interesting photophysical properties, showing vibronically resolved emission spectra at room temperature in CH₂Cl₂, resembling a ligand localized emission profile. The photophysics and ¹O₂ sensitization experiments support a triplet state assignment for these emissions which are best described as an admixture of charge transfer and ligand localized components, which decay symmetrically with time as evidenced by time resolved emission spectra. Room temperature ligand-localized fluorescence emission is observed from the zinc complexes whereas phosphorescence emission from the ³π-π* manifold was obtained at 77 K in 4 : 1 EtOH/MeOH matrices doped with 10% ethyl iodide. Compounds 1 and 2 display long-lived emission at room temperature, the latter possessing a longer lifetime, higher quantum yield, and longer wavelength emission. Lowering the temperature from 298 K to 77 K induces an increase in the excited state lifetime of both platinum systems together with a blue shift in their respective emission maxima, concomitant with more pronounced vibronic structure. The data are consistent with configurationally mixed triplet excited states at room temperature which persists in 77 K glasses. The corresponding Zn(II) complexes display significantly higher energy ligand-localized phosphorescence at 77 K. This latter result suggests that the nature of the metal and/or coordination environment imparts a significant electronic perturbation into the ligand-localized triplet states of these conjugated terpyridyl structures.



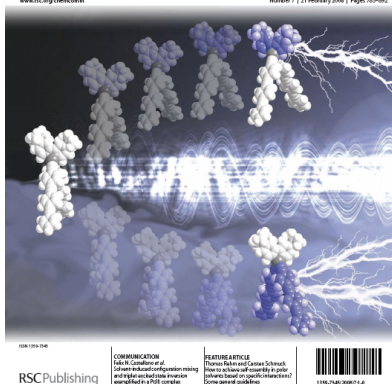
Noncoherent Low-Power Upconversion in Solid Polymer Films. Islangulov, R.R.; Lott, J.; Weder, C.; Castellano, F.N. *J. Am. Chem. Soc.* **2007**, 129, 12652-12653.



Noncoherent low-power photon upconversion has been realized in solid thin films composed of an ethyleneoxide/epichlorohydrin copolymer doped with palladium octaethylporphyrin (PdOEP) and 9,10-diphenylanthracene (DPA). Selective excitation of PdOEP at 544 nm generates easily visualized DPA fluorescence in the blue with noncoherent light sources under ambient laboratory conditions. The incident excitation power dependence is quadratic in nature, exemplifying that sequential one-photon absorption by PdOEP leads to the sensitization of two triplet DPA chromophores, which in turn annihilate to produce the upconverted singlet DPA fluorescence. Time-resolved emission experiments confirm that the solid host facilitates these sequential bimolecular reactions leading to delayed DPA fluorescence; however, these processes are notably slower than the analogous photochemistry in fluid solution.

Solvent-Induced Configuration Mixing and Triplet Excited State Inversion Exemplified in a Pt(II) Complex. Goeb, S.; Rachford, A.A.; Castellano, F.N. *Chem. Commun.* **2008**, 814-816. (*Chemical Communications* Cover Issue 7, 2008)

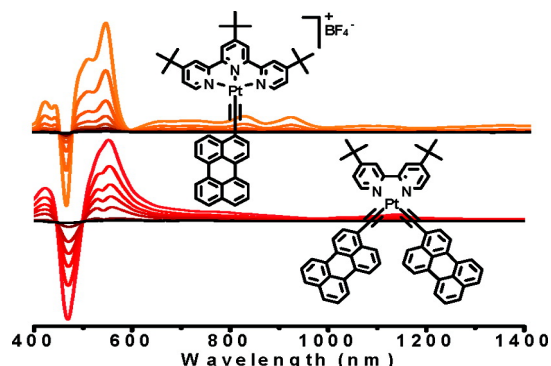
The present study provides clear-cut experimental evidence for solvent-induced configuration mixing and complete triplet state inversion at room temperature in a Pt(II) charge transfer complex bearing a combination of energetically proximate charge transfer and intraligand triplet excited states.



Pd^{II} Phthalocyanine-Sensitized Triplet-Triplet Annihilation from Rubrene. Singh-Rachford, T.N.; Castellano, F.N. *J. Phys. Chem. A* **2008**, *112*, 3550-3556.

Upconverted yellow singlet fluorescence from rubrene (5,6,11,12-tetraphenylnaphthacene) was generated from selective excitation ($\lambda_{\text{ex}} = 725 \text{ nm}$) of the red light absorbing triplet sensitizer palladium(II) octabutoxyphthalocyanine, PdPc(OBu)₈, in vacuum degassed toluene solutions using a Nd:YAG/OPO laser system in concert with gated iCCD detection. The data are consistent with upconversion proceeding from triplet-triplet annihilation (TTA) of rubrene acceptor molecules. The TTA process was confirmed by the quadratic dependence of the upconverted delayed fluorescence intensity with respect to incident light, measured by integrating the corresponding kinetic traces as a function of the incident excitation power. In vacuum degassed toluene solutions, the red-to-yellow upconversion process is stable under continuous long wavelength irradiation and is readily visualized by the naked eye even at modest laser fluence (0.6 mJ/pulse). In aerated solutions, however, selective excitation of the phthalocyanine sensitizer leads to rapid decomposition of rubrene into its corresponding endoperoxide as evidenced by UV-vis (in toluene), ¹H NMR (in d⁶-benzene), and MALDI-TOF mass spectrometry, consistent with the established reactivity of rubrene with singlet dioxygen. The upconversion process in this triplet sensitizer/acceptor-annihilator combination was preliminarily investigated in solid polymer films composed of a 50:50 mixture of an ethyleneoxide/epichlorohydrin copolymer, P(EO/EP). Films that were prepared under an argon atmosphere and maintained under this inert environment successfully achieve the anticipated quadratic incident power dependence, whereas air exposure causes the film to deviate somewhat from this dependence. To the best of our knowledge, the current study represents the first example of photon upconversion using a phthalocyanine triplet sensitizer, furthering the notion that anti-Stokes light-producing sensitized TTA appears to be a general phenomenon as long as proper energy criteria are met.

Ligand Localized Excited States in Platinum(II) Bipyridyl and Terpyridyl Peryleneacetylides. Rachford, A.A.; Goeb, S.; Ziesel, R.; Castellano, F.N. *Inorg. Chem.* **2008**, *47*, 4348-4355.

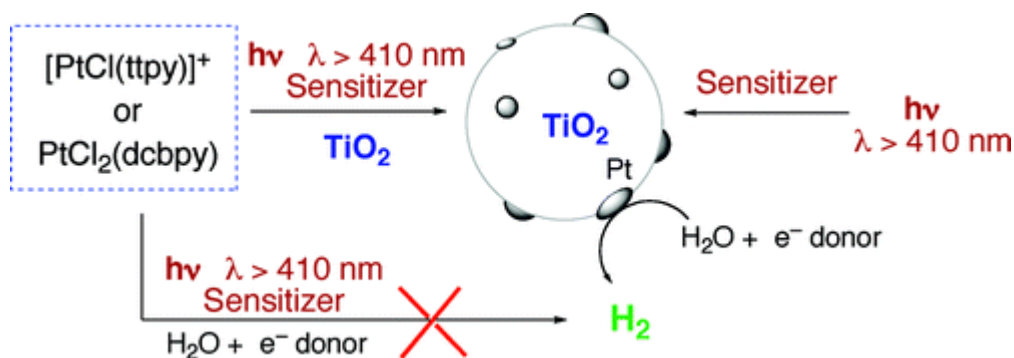


An investigation of the photophysics of two complexes, $[\text{Pt}(\text{tBu}_3\text{tpy})(\text{C}\equiv\text{C}\text{-perylene})]\text{BF}_4$ (**1**) and $\text{Pt}(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}\text{-perylene})_2$ (**2**), where tBu_3tpy is 4,4',4''-tri(*tert*-butyl)-2,2':6',2''-terpyridine, tBu_2bpy is 4,4'-di(*tert*-butyl)-2,2'-bipyridine, and $\text{C}\equiv\text{C}\text{-perylene}$ is 3-ethynylperylene, reveals that they both exhibit perylene-centered ligand localized excited triplet states (^3IL) upon excitation with visible light. These complexes do not display any significant photoluminescence at room temperature but readily sensitize $^1\text{O}_2$ in aerated CH_2Cl_2 solutions, as evidenced by its characteristic emission near 1270 nm. The transient absorption difference spectra were compared to bi- and tridentate phosphine peryleneacetylides intended to model the ^3IL peryleneacetylide excited states in addition to the related phenylacetylide-bearing polyimine analogues, with the latter model being the respective triplet charge-transfer (^3CT) excited states. The transient difference spectra of the two title compounds display excited-state absorptions largely attributable to perylene localized ^3IL states yet exhibit somewhat attenuated excited-state lifetimes relative to those of the phosphine model chromophores. The abbreviated lifetimes in **1** and **2** may suggest the involvement of the energetically proximate ^3CT triplet state exerting an influence on excited-state decay, and the effect appears to be stronger in **1** relative to **2**, consistent with the energies of their respective ^3CT states.

Photochemical Upconversion Approach to Broad-Band Visible Light Generation. Singh-Rachford, T.N.; Islangulov, R.R.; Castellano, F.N. *J. Phys. Chem. A* **2008**, *112*, 3906-3910.

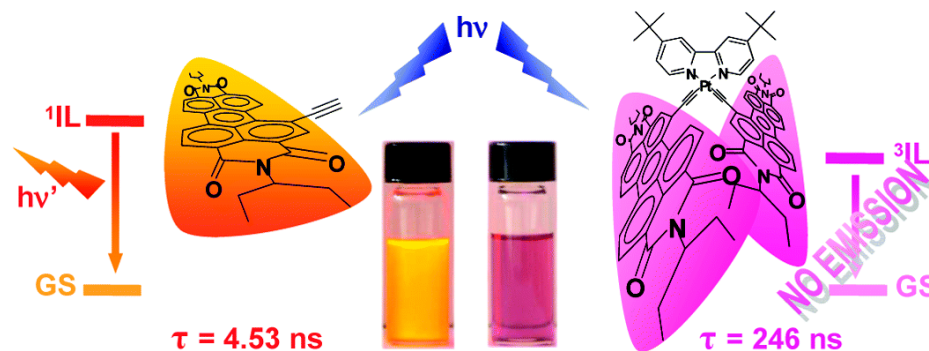
The sensitized triplet-triplet annihilation (TTA) of 9,10-dimethylantracene (DMA) upon selective excitation of $[\text{Ru}(\text{dmb})_3]^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine) at 514.5 nm in dimethylformamide (DMF) resulted in upconverted and downconverted DMA excimer photoluminescence. The triplet excited state of $[\text{Ru}(\text{dmb})_3]^{2+}$ is efficiently quenched by 11 mM DMA in DMF resulting in photon upconversion but no excimer formation. The bimolecular quenching constant of the dynamic quenching process is $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. At 90 mM DMA, both upconversion and downconversion processes are readily observed in aerated DMF solutions. The TTA process was confirmed by the quadratic dependence of the upconverted and downconverted emission emanating from the entire integrated photoluminescence profile (400–800 nm) of DMA measured with respect to incident light power. Time-resolved emission spectra of $[\text{Ru}(\text{dmb})_3]^{2+}$ and 90 mM DMA in both aerated and deaerated DMF clearly illustrates the time-delayed nature of both types of singlet-state emission, which interestingly shows similar decay kinetics on the order of 14 μs . The emission quantum yields (Φ) measured using relative actinometry increased with increasing DMA concentrations, reaching a plateau at 3.0 mM DMA ($\Phi = 4.0\%$), while at 90 mM DMA, the overall quantum yield diminished to 0.5%. The dominant process occurring at 3.0 mM DMA is upconversion from the singlet excited state of DMA, whereas at 90 mM DMA, both upconversion and excimeric emission are observed in almost equal portions, thereby resulting in an overall broad-band visible light-emission profile.

Bi- and Terpyridyl Platinum(II) Chloro Complexes: Molecular Catalysts for the Photogeneration of Hydrogen from Water or Simply Precursors for Colloidal Platinum? Du, P.; Schnieder, J. Zhao, W.; Patel, U.; Castellano, F.N.; Eisenberg, R. *J. Am. Chem. Soc.* **2008**, *130*, 5056-5058.



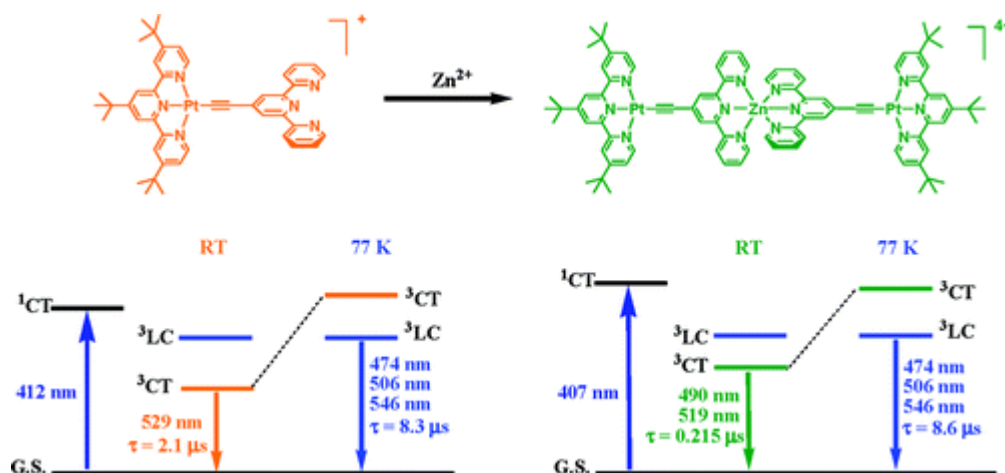
Platinum(II) bi- and terpyridyl chloro complexes, Pt(dcbpy)Cl_2 and $[\text{Pt(tpy)Cl}]^+$, where dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine and ttpy = 4-tolyl-2,2':6',2''-terpyridine, are used to investigate the nature of the active catalyst for the photocatalytic production of hydrogen from water. In a Pt(II) chloro system that contains a sacrificial electron donor, either MeOH or triethanolamine (TEOA), and titanium dioxide (TiO_2) as an electron relay, sizable amounts of H_2 can be observed upon UV bandgap irradiation. The quantity of H_2 can be significantly reduced in the presence of mercury under the same conditions. Using a known sensitizer, $[\text{Pt(tpy)(phenylacetylide)}]^+$ (1), combined with a Pt(II) chloro complex in a similar system, there is a substantial induction period until the evolution of H_2 , under visible light ($\lambda > 410 \text{ nm}$) irradiation. It is suggested that the Pt(II) chloro complexes are simply acting as precursors to Pt colloids that function as the H_2 generating catalyst.

Accessing the Triplet Excited State in Perylenediimides. Rachford, A.A.; Goeb, S.; Castellano, F.N. *J. Am. Chem. Soc.* **2008**, 130, 2766-2767.



Here, we present a strategy designed to permit access to the PDI triplet manifold that preserves the desirable colorfastness and visible light-absorption properties associated with these dyes. To this end, three new Pt(II) complexes each bearing two PDI moieties tethered to the metal center via acetylide linkages emanating from one of the PDI bay positions have been synthesized, structurally characterized, and thoroughly examined by nanosecond laser flash photolysis. Upon ligation, the bright singlet-state fluorescence of the PDI chromophore is quantitatively quenched, and no long wavelength photoluminescence is observed from the Pt(II)-PDI complexes in deaerated solutions. In each of the Pt-PDI chromophores, quantitatively similar transient absorption difference spectra were obtained; the only distinguishing characteristic is in their single-exponential lifetimes ($\tau = 246 \text{ ns}$, $1.0 \mu\text{s}$, and 710 ns). Triplet-state sensitization experiments of “free” PDI-CCH using thioxanthone confirmed the PDI triplet state assignments in each of the Pt-PDI structures.

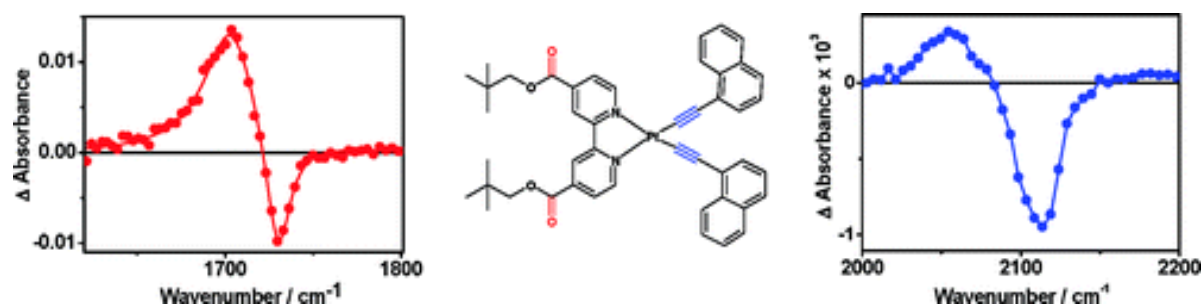
Photophysics of the Platinum(II) Terpyridyl Terpyridylacetylide Platform and the Influence of Fe(II) and Zn(II) Coordination. Muro, M.L.; Diring, S.; Wang, X.; Ziesel, R.; Castellano, F.N. *Inorg. Chem.* **2008**, 47, 6796-6803.



The synthesis, structural characterization, and photoluminescence (PL) properties of the square-planar terpyridylplatinum(II) complex $[Bu_3tpyPtCCtpy]^+$ (**1**) and the octahedral trinuclear Fe^{II} and Zn^{II} analogues $[Fe(Bu_3tpyPtCCtpy)_2]^{4+}$ (**2**) and $[Zn(Bu_3tpyPtCCtpy)_2]^{4+}$ (**3**) are described. The photophysical properties of the mononuclear Pt^{II} complex **1** are consistent with a charge-transfer excited-state parentage producing a large Stokes shift with a concomitant broad, structureless emission profile. The Fe -based ligand-field states in **2** provide an efficient nonradiative deactivation pathway for excited-state decay, resulting in a nonemissive compound at room temperature. Interestingly, upon chelation of **1** with Zn^{II} , a higher energy charge-transfer emission with a low-energy shoulder and a 215 ns excited-state lifetime is produced in **3**. A spectroscopically identical species relative to **3** was produced in control experiments when **1** was

reacted with excess protons (HClO_4) as ascertained by UV-vis and static PL spectra measured at room temperature and 77 K. Therefore, the chelation of Zn^{II} to **1** is acid-base in nature, and its Lewis acidity renders the highest occupied molecular orbital level in **1** much less electron-rich, which induces a blue shift in both the absorption and emission spectra. At 77 K, complexes **1**, **3**, and protonated **1** display at least one prevalent vibronic component in the emission profile (1360 cm^{-1}) resembling PL emanating from a ligand-localized excited-state, indicating that these emitting states are inverted relative to room temperature. These results are qualitatively confirmed by the application of time-dependent theory using only the 1360 cm^{-1} mode to reproduce the low-temperature emission spectra.

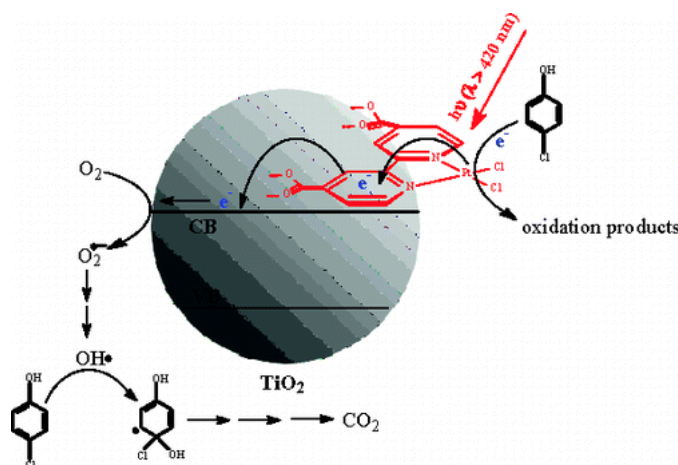
Ultrafast Excited State Dynamics in Pt(II) Chromophores Bearing Multiple IR Absorbers. Glik, E.A.; Kinayyigit, S.; Ronayne, K.; Towrie, M.; Sazanovich, I.V.; Weinstein, J.A.; Castellano, F.N. *Inorg. Chem.* **2008**, 47, 6974-6983.



The paper reports the synthesis, structural characterization, electrochemistry, ultrafast time-resolved infrared (TRIR) and transient absorption (TA) spectroscopy associated with two independent d^8 square planar $\text{Pt}(\text{II})$ diimine chromophores, $\text{Pt}(\text{dnpebpy})\text{Cl}_2$ (**1**) and $\text{Pt}(\text{dnpebpy})(\text{CCnaph})_2$ (**2**), where $\text{dnpebpy} = 4,4'-(\text{CO}_2\text{CH}_2-t\text{Bu})_2-2,2'$ -bipyridine and $\text{CCnaph} = \text{naphthylacetylide}$. The neopentyl ester substitutions provided markedly improved complex solubility relative to the corresponding ethyl ester which facilitates synthetic elaboration as well as spectroscopic investigations. Following 400 nm pulsed laser excitation in CH_2Cl_2 , the 23 cm^{-1} red shift in the ν_{CO} vibrations in **1** are representative of a complex displaying a lowest charge-transfer-to-diimine (CT) excited state. The decay kinetics in **1** are composed of two time constants assigned to vibrational cooling of the ^3CT excited-state concomitant with its decay to the ground state ($\tau = 2.2 \pm 0.4\text{ ps}$), and to cooling of the formed vibrationally hot ground electronic state ($\tau = 15.5 \pm 4.0\text{ ps}$); we note that an assignment of the latter to a ligand field state cannot be excluded. Ultrafast TA data quantitatively support these assignments yielding an excited-state lifetime of $2.7 \pm 0.4\text{ ps}$ for the ^3CT excited-state of **1** and could not detect any longer-lived species. The primary intention of this study was to develop a Pt^{II} complex (**2**) bearing dual infrared spectroscopic tags (CC attached to the metal and CO (ester) attached to the diimine ligand) to independently track the movement of charge density in different

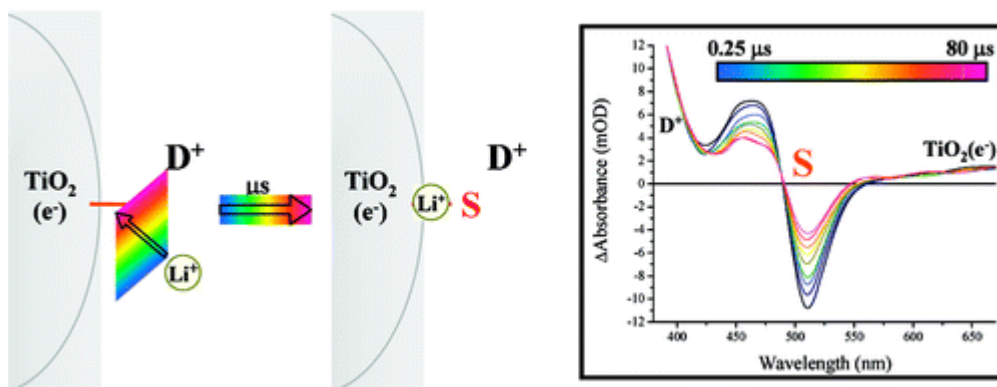
segments of the molecule following pulsed light excitation. Femtosecond laser excitation of **2** in CH₂Cl₂ at 400 nm simultaneously induces a red-shift in both the ν_{CO} ($\sim 30\text{ cm}^{-1}$) and the ν_{CC} ($\sim 61\text{ cm}^{-1}$) vibrations. The TRIR data in **2** are consistent with a charge transfer assignment, and the significant decrease of the energy of the ν_{CC} vibration suggests a considerable contribution from the acetylide ligands in the highest occupied molecular orbital. Therefore, we assign the lowest energy optical transitions in **2** as a combination of metal-to-ligand and ligand-to-ligand charge transfers. The excited-state of **2** is emissive at RT, with an emission maximum at 715 nm, quantum yield of 0.0012, and lifetime of 23 ns.

Visible-Light Induced Water Detoxification Catalyzed by Pt^{II} Dye Sensitized Titania. Zhao, W.; Sun, Y.; Castellano, F.N. *J. Am. Chem. Soc.* **2008**, 130, 12566-12567.



A new dye sensitization system incorporating Pt(dcbpy)Cl₂ on Degussa P-25 TiO₂ for the photomineralization of aqueous organic pollutants under visible light irradiation is described. The representative wastewater pollutant, 4-chlorophenol (4-CP), is readily oxidized (ultimately to CO₂) when the Pt^{II} dye sensitized TiO₂ is exposed to visible light in the presence of dissolved O₂, and the reaction is accelerated when the solution is purged with O₂ gas at 1 atm. The sensitizer is regenerated during the photocatalysis; therefore, 4-CP effectively reduces the oxidized form of the surface bound dye. The experimental data are consistent with parallel oxidative decomposition pathways for 4-CP, one which operates using conduction band electrons to produce hydroxyl radicals and another where the oxidized sensitizer irreversibly oxidizes 4-CP.

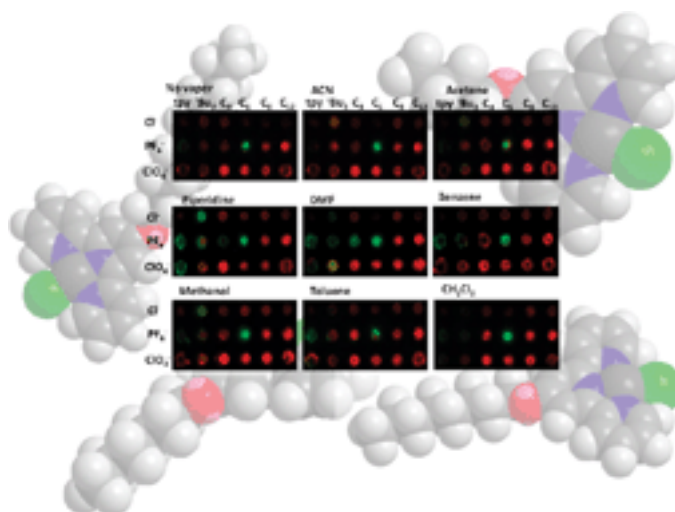
Slow Cation Transfer Follows Sensitizer Regeneration at Anatase TiO₂ Interfaces. Staniszewski, A.; Ardo, S.; Sun, Y.; Castellano, F.N.; Meyer, G.J. *J. Am. Chem. Soc.* **2008**, *130*, 11586-11587.



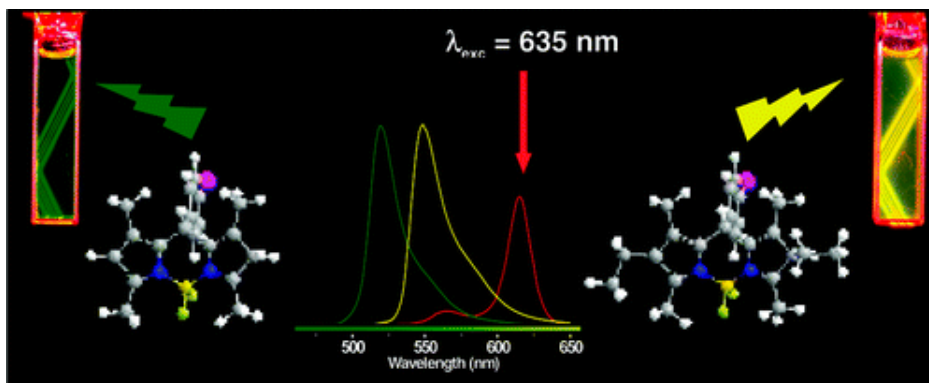
After rapid photoinduced electron injection into TiO₂ and regeneration by a donor, D, such as iodide or phenothiazine, sensitizers are present in an environment distinctly different from that prior to light absorption. Significantly, the absorption spectrum of the Ru(II) sensitizer in this new environment is one that is known to be less favorable for excited-state electron injection. The transient absorption features were found to report on photoinduced variations in the local electronic environment of the Ru(II) sensitizer–TiO₂ interface that were induced by ion transfer. The data demonstrate that slow (μs to ms) cation transfer follows regeneration to yield the sensitizer that was initially photoexcited.

Microarray Pattern Recognition based on Pt^{II} Terpyridyl Chloride Complexes: Vapochromic and Vapoluminescent Response. Muro, M.L.; Daws, C.A.; Castellano, F.N. *Chem. Commun.* **2008**, 6134-6136.

Eighteen distinct Pt^{II} terpyridyl chloride cross-reactive sensor elements incorporated into microarrays with 1000 × 250 μm well dimensions generate distinctive colorimetric and luminometric responses upon exposure to a variety of volatile organic compounds (VOCs).

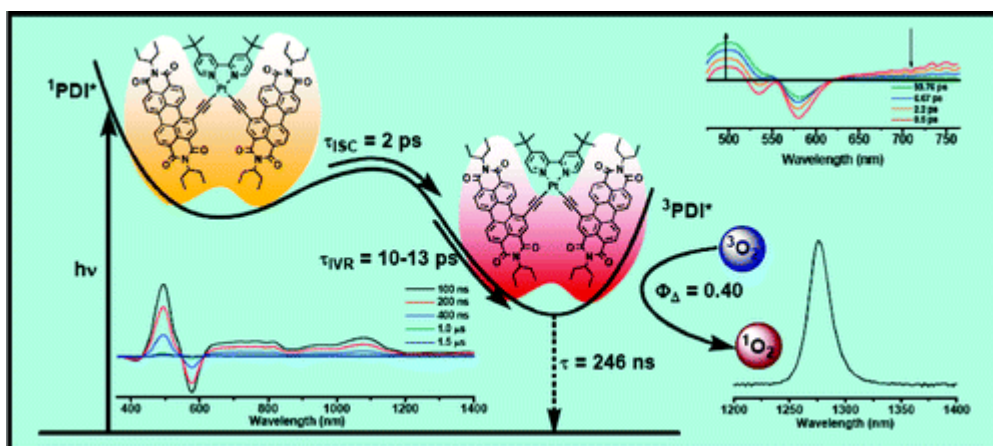


Boron Dipyrrromethene Chromophores: Next Generation Triplet Acceptors/Annihilators for Low Power Upconversion Schemes. Singh-Rachford, T.N.; Haefele, A.; Ziesel, R.; Castellano, F.N. *J. Am. Chem. Soc.* **2008**, 130, 16164-16165.



In the present study, the red-light absorbing platinum(II) tetraphenyltetrabenzoporphyrin (PtTPBP) was used as a triplet sensitizer in conjunction with two distinct iodophenyl-bearing BODIPY derivatives independently serving as triplet acceptors/annihilators poised for photon upconversion based on triplet-triplet annihilation. In deaerated benzene solutions, extremely stable and high quantum efficiency green ($\Phi_{UC} = 0.0313 \pm 0.0005$) and yellow ($\Phi_{UC} = 0.0753 \pm 0.0036$) upconverted emissions were observed from selective red excitation of the PtTPBP sensitizer at 635 ± 5 nm. The current systems represent the first examples of photon upconversion where aromatic hydrocarbons do not serve the role of triplet acceptor/annihilator. Notably, the nature of the current chromophore compositions permitted highly reproducible upconversion quantum efficiency determinations while permitting the evaluation of the triplet-triplet annihilation quantum yields in both instances.

Evolution of the Triplet Excited State in Pt^{II} Perylenediimides. Danilov, E.O.; Rachford, A.A. Goeb, S.; Castellano, F.N. *J. Phys. Chem. A* **2009**, 113, 5763-5768.

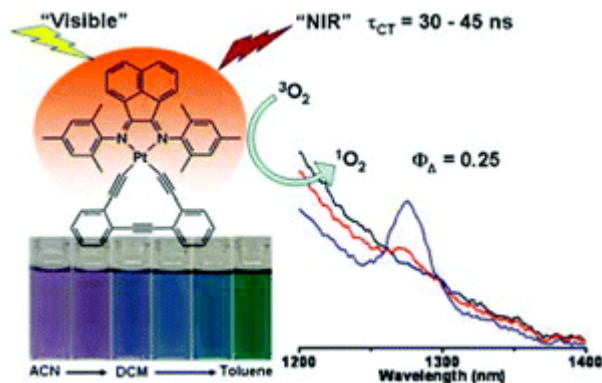


Here, we present the ultrafast dynamics of a series of metal complexes developed to permit access to the perylenediimide (PDI) triplet manifold that preserves the desirable colorfastness and visible light-absorption properties associated with these dyes. To this end, three Pt^{II} complexes each bearing two PDI moieties tethered to the metal center through acetylide linkages emanating from one of the PDI bay positions have been thoroughly examined by static spectroscopic methods, electrochemistry, laser flash photolysis, and ultrafast transient absorption spectrometry. Upon ligation to the Pt^{II} center, the bright singlet-state fluorescence ($\Phi = 0.91$, $\tau = 4.53$ ns) of the free PDI-CCH chromophore is quantitatively quenched, and no long wavelength photoluminescence is observed from any of the Pt^{II}-PDI complexes in deaerated solutions. Ultrafast transient measurements reveal that upon ligation of PDI-CCH to the Pt^{II} center, picosecond intersystem crossing ($\tau = 2-4$ ps) from the ¹PDI excited state is followed by vibrational

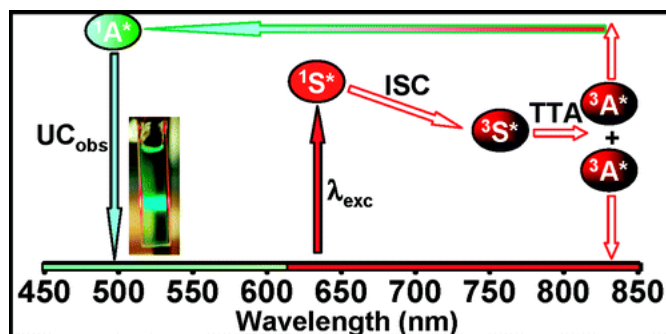
cooling ($\tau = 12\text{--}19$ ps) of the hot ^3PDI excited state, whereas only singlet-state dynamics, including stimulated emission, were observed in the “free” PDI–CCH moiety. In each of the Pt–PDI chromophores, quantitatively similar transient absorption difference spectra were obtained; the only distinguishing characteristic is in their single-exponential lifetimes ($\tau = 246$ ns, 1.0 μs , and 710 ns). These long-lived ^3PDI excited states are clearly poised for bimolecular electron and energy transfer schemes. In the present case, the latter is demonstrated through bimolecular sensitization of singlet oxygen phosphorescence at ~ 1270 nm in aerated dichloromethane solutions, producing reasonable $^1\text{O}_2$ quantum yields ($\Phi_{\Delta} = 0.40\text{--}0.55$) across this series of molecules.

[Pt(mesBIAN)(tda)]: A Near-Infrared Emitter and Singlet Oxygen Sensitizer. Rachford, A.A.; Hua, F.; Adams, C.J.; Castellano, F.N. *Dalton Trans.* **2009**, 3950–3954.

The synthesis and subsequent photophysical investigation of $[\text{Pt}(\text{mesBIAN})(\text{tda})]$, where mesBIAN is bis(mesitylimino)acenaphthene and tda is tolan-2,2'-diacetylide, reveal excited-state characteristics best described as triplet charge transfer (^3CT) in nature upon visible light excitation. Large ground-state dipole moments are apparent as the absorption spectrum dramatically red-shifts with decreasing solvent polarity. The ^3CT excited state is significantly lower in energy than the ligand-centered ^3tda excited-state, as confirmed by steady-state and time-resolved techniques. Singlet oxygen sensitization studies demonstrate that $^1\text{O}_2$ production occurs by diffusive quenching from the photo-excited ^3CT state ($\Phi_{\Delta} = 0.24$, $\lambda_{\text{max}} \sim 1270$ nm) in oxygen-saturated dichloromethane.

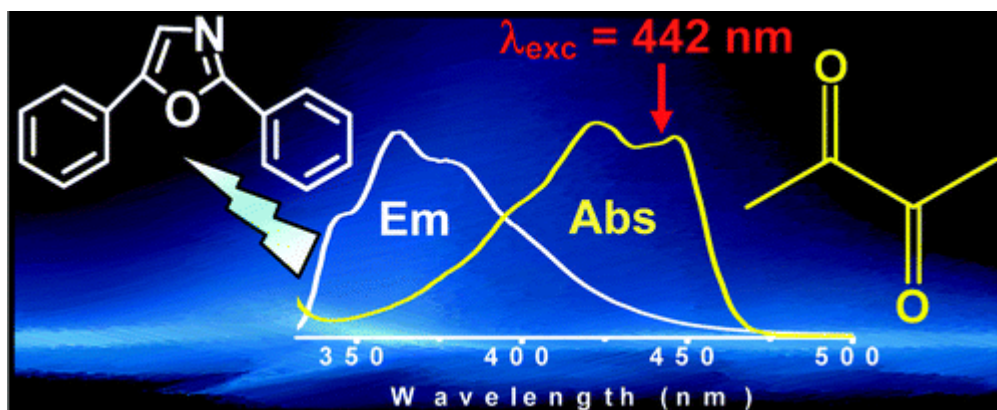


Supra-nanosecond Dynamics of a Red-to-Blue Photon Upconversion System. Singh-Rachford, T.N.; Castellano, F.N. *Inorg. Chem.* **2009**, 48, 2541-2548.



Blue-green upconverted emission from 2-chloro-*bis*-phenylethynylantracene (2CBPEA) sensitized by the red-absorbing platinum(II)tetraphenyltetrabenzoporphyrin (PtTPBP) has been investigated in *N,N*-dimethylformamide (DMF). The upconverted singlet fluorescence of 2CBPEA resulting from its sensitized triplet-triplet annihilation (TTA) is observed following selective excitation of PtTPBP at 635 ± 5 nm. Stern-Volmer analysis of the photoluminescence quenching of PtTPBP by 2CBPEA yields a bimolecular quenching constant of $1.62 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, slightly below the diffusion limit in DMF at room temperature. The TTA process was confirmed by the quadratic dependence of the integrated upconverted singlet fluorescence emission profile of 2CBPEA measured as a function of 635 nm incident laser power. Time-resolved emission spectra following 630 nm nanosecond laser pulses illustrate the prompt nature of porphyrin phosphorescence quenching and the delayed nature of the upconverted singlet fluorescence from 2CBPEA. Transient absorption decays monitored at the peak of the characteristic 2CBPEA triplet-triplet excited-state absorption (490 nm) measured as a function of incident nanosecond 630 nm pump laser fluence recovered the rate constant for the sensitized TTA process, $k_{\text{TT}} = 5.64 \pm 0.08 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. To calculate this rate constant, we determined the triplet-triplet extinction coefficient of 2CBPEA ($12,500 \text{ M}^{-1} \text{ cm}^{-1}$ at 490 nm) utilizing triplet energy transfer from donors with known excited-state extinction coefficients, namely $[\text{Ru}(\text{bpy})_3]^{2+}$ and 2-acetonaphthone and averaged these values. The current work, to the best of our knowledge, represents the first example of red-to-blue upconversion thus demonstrating another viable sensitized TTA process, as well as providing the first measurements of k_{TT} in a photon upconverting scheme. As 2CBPEA is stable under ambient conditions, this chromophore represents an almost ideal candidate for light-producing sensitized TTA in aerated polymeric materials, and we demonstrate successful translation of the present donor-acceptor/annihilator system into a low T_g polyurethane.

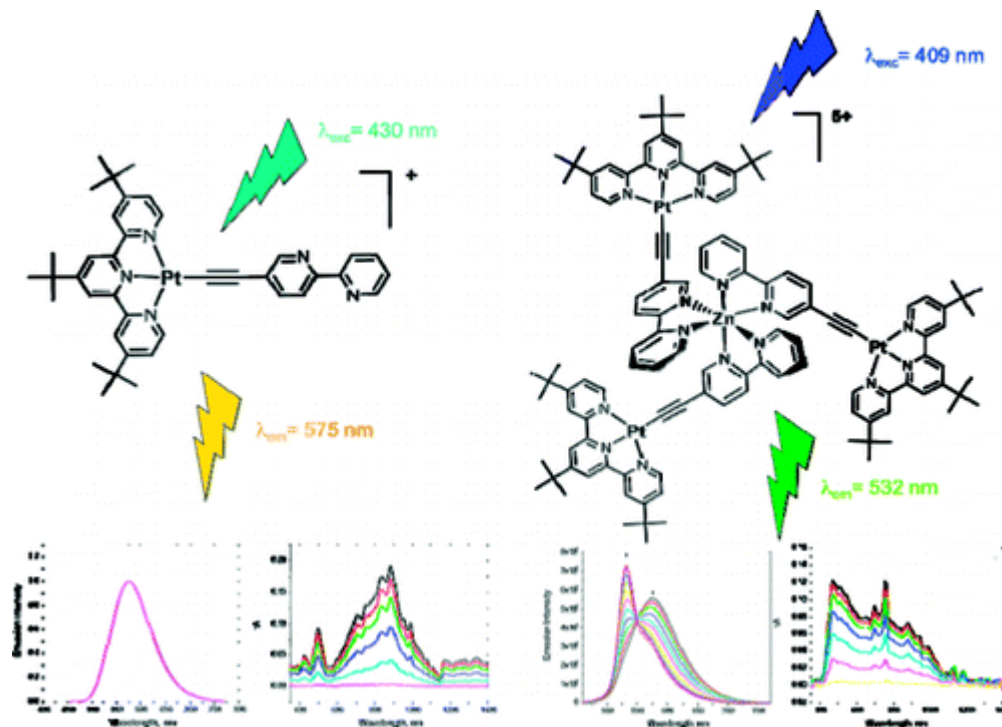
Low Power Visible-to-UV Upconversion. Singh-Rachford, T.N.; Castellano, F.N. *J. Phys. Chem. A* **2009**, 113, 5912-5917.



Low power visible-to-UV photon upconversion is demonstrated for the first time, achieved from two simple organic chromophores dissolved in benzene. Selective 442 nm excitation of the triplet sensitizer 2,3-butanedione (biacetyl) in the presence of the laser dye 2,5-diphenyloxazole (PPO) results in the observation of singlet fluorescence from the latter in the UV centered at 360 nm, anti-Stokes shifted by a record 0.64 eV with respect to the excitation. All of the experimental data are consistent with the upconverted singlet PPO fluorescence being produced as a result of biacetyl-sensitized triplet-triplet annihilation (TTA) of triplet excited PPO chromophores. Nanosecond laser flash photolysis performed under pseudo-first-order conditions revealed the bimolecular rate constant of triplet-triplet energy transfer between the biacetyl sensitizer and PPO acceptor, $k_q = 9.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The TTA process was confirmed by the quadratic dependence of the upconverted integrated PPO emission intensity measured with respect to incident 442 nm light power density. The maximum quantum yield of the upconverted emission (0.0058 ± 0.0002) was determined relative to 1,8-diphenyl-1,3,5,7-octatetraene, both measured with 0.389 W/cm^2 incident power density. The PPO triplet-triplet annihilation rate constant (k_{TT}) was determined from transient absorption decays monitored at the peak of its characteristic triplet-to-triplet excited-state absorption (500 nm) as a function of incident pulsed laser fluence; this process attains the diffusion limit in benzene at room temperature, $k_{\text{TT}} = 1.1 \pm 0.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

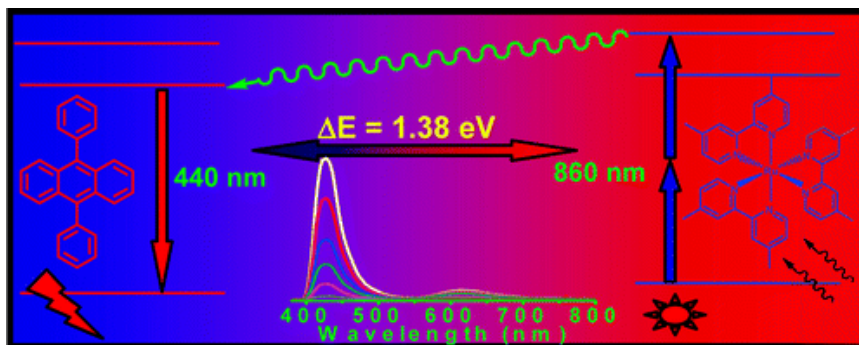
Solvent-induced Configuration Mixing and Triplet Excited State Inversion: Insights from Transient Absorption and Transient DC Photoconductivity Measurements. She, C.; Rachford, A.A.; Wang, X.; Goeb, S.; El-Ballouli, A.O.; Castellano, F.N.; Hupp, J.T. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8586-8591.

Solvent-induced excited-state configuration mixing in a Pt(II) diimine chromophore with phenylene ethynylene containing acetylide ligands, $[\text{Pt}(\text{Bu}_2\text{bpy})(\text{PE}3)_2]$ (1), was characterized by nanosecond transient absorption spectroscopy and transient dc photoconductivity (TDCP). The mixing is a result of closely spaced triplet charge transfer (^3CT) and intraligand-localized (^3IL) triplet energy levels that are finely tuned with solvent polarity as ascertained by their parent model chromophores $[\text{Pt}(\text{Bu}_2\text{bpy})(\text{PE}1)_2]$ (2) and $[\text{Pt}(\text{P}2)(\text{PE}3)_2]$ (3), respectively. The absorption difference spectrum of the mixed triplet state is dramatically different from those of the ^3CT and ^3IL state model chromophores. The ^3CT , ^3IL and configuration-mixed triplet states led to distinct TDCP signals. The TDCP response is of negative polarity for ^3CT excited states but of positive polarity for ^3IL excited states. TDCP transients for 1 in mixed solvents are a combination of signals from the ^3IL and ^3CT states, with the signal magnitude depending on the polarity of solvent composition. The fraction of ^3CT state character in the configurationally mixed excited state was quantified by TDCP to be ~ 0.24 in pure benzene, while it decreased to ~ 0.05 in 20 : 80 (v : v) benzene- CH_2Cl_2 . The charge transfer fraction appears to increase slightly to ~ 0.11 in the lower polarity 20 : 80 *n*-hexane- CH_2Cl_2 medium. TDCP is shown to be a useful tool for the identification of the lowest excited state in electrically neutral metal-organic chromophores.



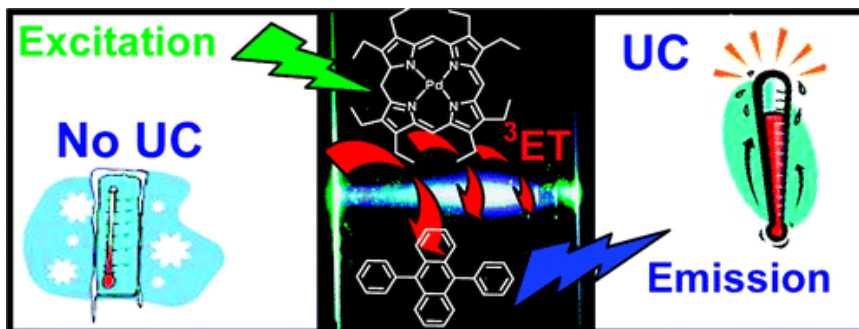
The synthesis, structural characterization, photoluminescence, and excited state absorption properties of a series of platinum(II) terpyridyl complexes bearing a bipyridyl acetylide subunit are presented. The $[\text{Bu}_3\text{tpyPtC}\equiv\text{Cbpy}]^+$ (**1**) complex displays a broad and structureless emission profile at room temperature (RT), a lifetime of 5.8 μs , and transient absorption (TA) difference spectra characteristic of a charge transfer (CT) excited state. Upon coordination of Fe^{2+} to **1**, producing tetranuclear **2**, the CT emission was quantitatively quenched presumably through the low-lying iron-based ligand field states present. Surprisingly, the addition of Zn^{2+} to solutions of **1** produces a higher energy emissive state with a substantially longer excited state lifetime of 16.1 μs . The combined spectroscopic data measured for the zinc titration product (**3**) suggests that the overall excited state is dominated by a CT manifold, albeit at higher energy relative to **1**. The photophysics of a bis-phosphine complex bearing two *trans*-disposed bpy-acetylide subunits (**4**) produced a model chromophore possessing an intraligand triplet excited state with a lifetime of 26 μs at RT. The bipyridyl analogue of **1**, $^t\text{Bu}_2\text{bpyPt}(\text{C}\equiv\text{Cbpy})_2$ (**5**), was also prepared and its photophysics are consistent with a lowest CT parentage at RT. The 77 K emission spectra measured for complexes **1**, **3**, **4**, and **5** are all consistent with a triplet bpy-acetylide localized excited state; the E_{00} energies vary over a modest 344 cm^{-1} across the series. However, the shorter 77 K excited state lifetimes observed for **1**, **3**, and **5** in comparison to **4** suggests that the energetically proximate CT state in the former compounds significantly influences excited state decay at low temperature.

Nonlinear Photochemistry Squared: Quartic Light-Power Dependence Realized in Photon Upconversion. Singh-Rachford, T.N.; Castellano, F.N. *J. Phys. Chem. A* **2009**, 113, 9266-9269.



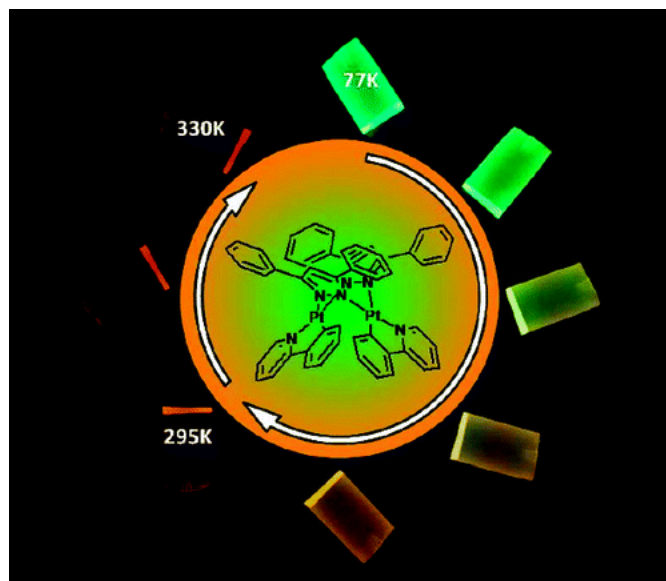
Simultaneous two-photon excitation of a solution mixture of $[\text{Ru}(\text{dmb})_3]^{2+}$ and 9,10-diphenylanthracene (DPA) using 860 nm light pulses from a Ti:Sapphire laser resulted in triplet energy transfer followed by triplet-triplet annihilation (TTA), ultimately leading to upconverted DPA fluorescence from the sensitized DPA triplets. The photochemistry sequence was confirmed by the unprecedented quartic (x^4) incident light power dependence exhibited by this process, which incidentally generated a record anti-Stokes shift of 1.38 eV for sensitized TTA.

Influence of Temperature on Low-Power Upconversion in Rubbery Polymers. Singh-Rachford, T.N.; Lott, J.; Weder, C.; Castellano, F.N. *J. Am. Chem. Soc.* **2009**, 131, 12007-12014.



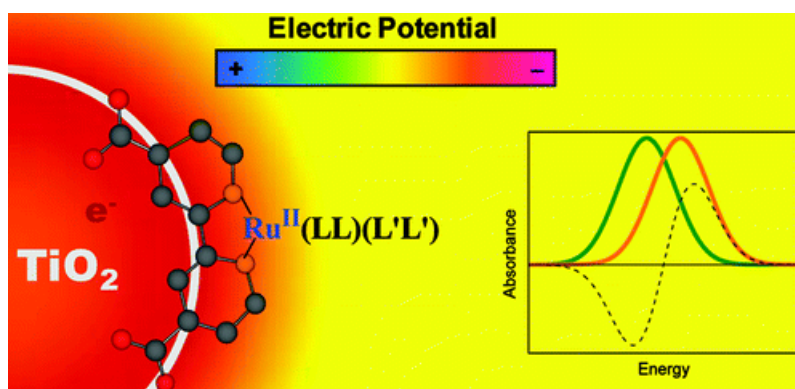
The upconverting properties of a dye cocktail composed of palladium(II) octaethylporphyrin (PdOEP, triplet sensitizer) and 9,10-diphenylanthracene (DPA, triplet acceptor/annihilator) were investigated as a function of temperature in several low glass transition temperature (T_g) polymer hosts including an ethyleneoxide-epichlorohydrin copolymer (EO-EPI) and the polyurethanes Texin 270, Texin 285, and Tecoflex EG-80A. Selective excitation of PdOEP at 544 nm in the presence of DPA in these materials resulted in anti-Stokes blue emission from DPA, a consequence of sensitized triplet-triplet annihilation (TTA) photochemistry, confirmed by the quadratic dependence of the upconverted fluorescence intensity with respect to incident light power. The upconversion process was completely suppressed by cooling a PdOEP/DPA blend film to below the T_g of the respective polymer. However, the blue emission was clearly visible by the naked eye upon heating these films to room temperature (290 K). Subsequently, the upconverted emission intensity increased with increasing temperature and was found to be completely reversible upon several heating and cooling cycles provided the temperature remained below 400 K. Heating samples above this temperature resulted in unrecoverable failure of the material to produce upconverted photons. The phosphorescence intensity decay of PdOEP in the polymer host, Tecoflex EG-80A, adequately fits to a sum of two exponential functions as well as the Kohlrausch-Williams-Watts (KWW) stretched exponential model. Increasing the temperature of the film increases the complexity and heterogeneity of the system as evidenced by the lower β values obtained from the KWW model as the temperature increases.

Thermochromic Absorption and Photoluminescence in [Pt(ppy)(μ-Ph₂pz)]₂. Rachford, A.A.; Castellano, F.N. *Inorg. Chem.* **2009**, 48, 10865-10867.



The temperature effects on the spectral properties and photophysics of a new d⁸-d⁸ dinuclear Pt^{II} chromophore, [Pt(ppy)(μ-Ph₂pz)]₂ (ppy is 2-phenylpyridine and Ph₂pz is 3,5-diphenylpyrazolate), have been investigated. The thermochromic shifts are tentatively ascribed to intramolecular σ interactions between the two pseudocofacial d_{z²} orbitals. Substantial emission profile changes occur in the solid state, solution, and doped polymer films.

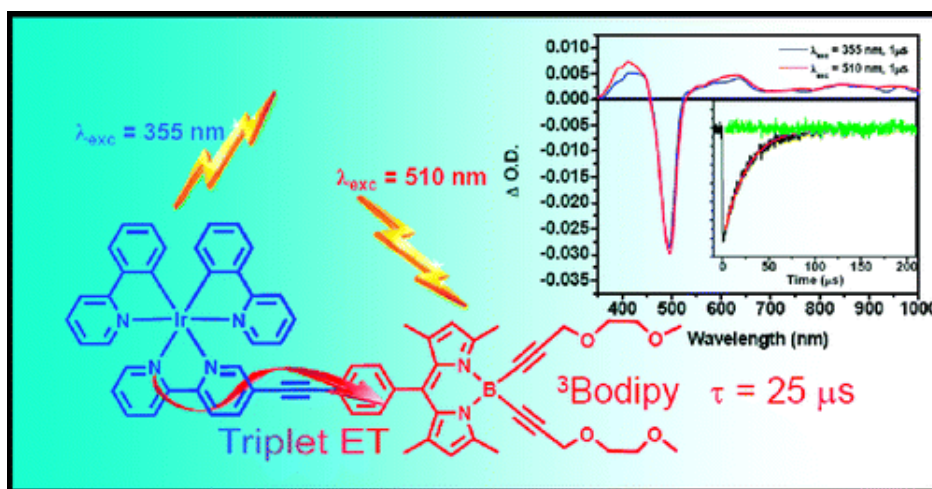
Stark Effects after Excited-State Interfacial Electron Transfer at Sensitized TiO₂ Nanocrystallites. Ardo, S.; Sun, Y.; Staniszewski, A.; Castellano, F.N.; Meyer, G.J. *J. Am. Chem. Soc.* **2010**, 132, 6696-6709.



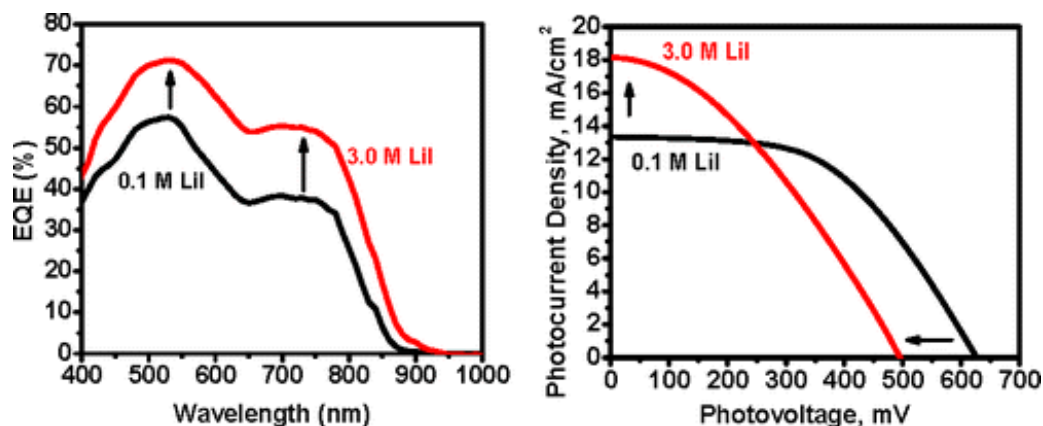
Photophysical studies were performed with [Ru(dtb)₂(dcb)](PF₆)₂ and *cis*-Ru(dcb)(dnb)(NCS)₂, where dtb is 4,4'-(C(CH₃)₃)₂-2,2'-bipyridine, dcb is 4,4'-(COOH)₂-2,2'-bipyridine, and dnb is 4,4'-(CH₃(CH₂)₈)₂-2,2'-bipyridine), anchored to anatase TiO₂ particles (~15 nm in diameter) interconnected in a mesoporous, 10 μm thick film immersed in Li⁺-containing CH₃CN electrolytes with iodide or phenothiazine donors. Pulsed-laser excitation resulted in rapid excited-state injection and donor oxidation to yield TiO₂(e⁻)s and oxidized donors, while the metal-to-ligand charge-transfer (MLCT) absorption spectrum of the Ru(II) coordination compounds differed from that which was initially excited. The spectral data were consistent with an underlying Stark effect and indicated that the surface electric field was not completely screened from the molecular sensitizer. The magnitude of the electric field was estimated to be ~270 MV/m from Li⁺ titration experiments, corresponding to a ~40 mV potential drop. With iodide donors, the amplitude of

the Stark effect decreased over time periods where charge recombination was absent, behavior attributed to “screening” of the electric field by interfacial ionic reorganization. The screening kinetics were nonexponential but were well described by the Kohlrausch–Williams–Watts model, from which a characteristic rate constant, τ_0^{-1} , of $\sim 1.5 \times 10^5 \text{ s}^{-1}$ was abstracted. At least seven other sensitizers and five different cations, as well as on SnO_2 nanoparticle films, exhibited similar transient absorption behavior with iodide donor molecules indicating that the effect was quite general. In the presence of phenothiazine donors (or in the absence of an external donor), there was no clear evidence for screening, and the Stark effect disappeared concurrent with interfacial charge recombination. Complementary spectroelectrochemical studies of these same sensitized films displayed similar absorption spectra when the TiO_2 thin film was partially reduced with a forward bias. Spectral modeling in the absence of donor molecules as well as studies of TiO_2 thin films sensitized with two different Ru(II) compounds demonstrated that the electric field created by excited-state injection from one sensitizer influenced the absorption spectra of other sensitizers that had not undergone photoinduced electron injection.

Boron Dipyrromethene (Bodipy) Phosphorescence Revealed in $[\text{Ir}(\text{ppy})_2(\text{bpy}-\text{C}\equiv\text{C}-\text{Bodipy})]^+$. Rachford, A.A.; Ziessel, R.; Bura, T.; Retailleau, P.; Castellano, F.N. *Inorg. Chem.* **2010**, 49, 3730-3736.

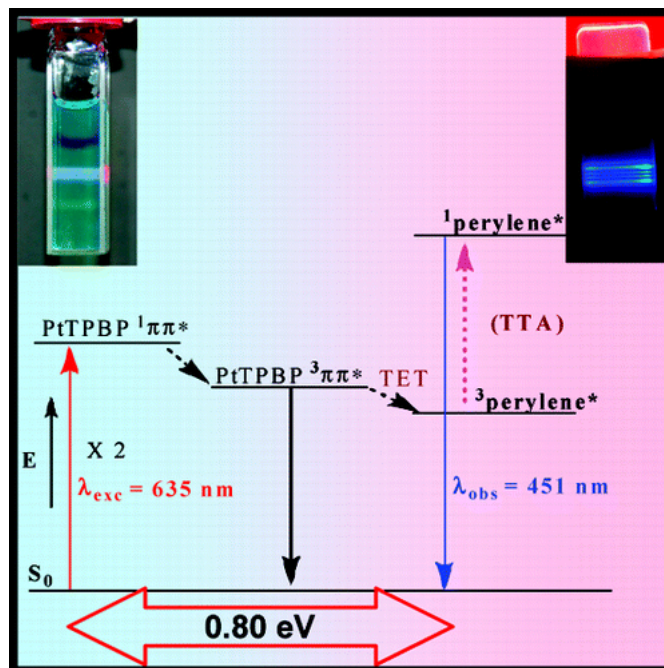


The synthesis, structural characterization, electrochemistry, and molecular photophysics of $[\text{Ir}(\text{ppy})_2(\text{bpy}-\text{C}\equiv\text{C}-\text{Bodipy})](\text{PF}_6)$, where ppy is 2-phenylpyridine and $\text{bpy}-\text{C}\equiv\text{C}-\text{Bodipy}$ is 5-ethynyl-2,2'-bipyridine-8-phenyl-1,3,5,7-tetramethyl-4,4-bis(2,5-dioxaoct-7-ynyl)-4-bora-3a,4a-diaza-s-indacene (**4**), is presented. Static and dynamic photoluminescence and absorption measurements in conjunction with cyclic voltammetry were employed to elucidate the nature of the intramolecular energy transfer processes occurring in the excited state of the title chromophore. Parallel studies were performed on appropriate model chromophores (**2** and **3**) intended to represent the photophysics of the isolated molecular subunits, that is, triplet metal-to-ligand-charge-transfer ($^3\text{MLCT}$) and triplet Bodipy intraligand (^3IL) excited states, respectively. Upon charge transfer excitation of the title chromophore, the $^3\text{MLCT}$ based phosphorescence readily observed in **2** ($\Phi_{\text{em}} = 0.027$, $\tau = 243 \text{ ns}$) is quantitatively quenched resulting from production of the $^3\text{Bodipy}$ excited state through intramolecular triplet–triplet energy transfer. The formation of the $^3\text{Bodipy}$ -localized excited state is confirmed by features in the transient absorption difference spectrum, extended excited-state lifetime ($\tau = 25 \mu\text{s}$), as well the observation of ^3IL Bodipy-based phosphorescence detected at 730 nm at 77 K. The low temperature Bodipy phosphorescence is readily produced in **4** as a result of the internal Ir(III) heavy atom.



This work focuses upon the effects of electrolyte composition, specifically the role of Li^+ and I^- ions, on the resultant photovoltaic performance of dye-sensitized solar cells (DSCs) based on a new Os(II) polypyridine complex of mixed denticity, $[\text{Os}(\text{Bu}_3\text{tpy})(\text{dcbpyH}_2)(\text{NCS})]\text{PF}_6$ (**1**). Photophysical and electrochemical characterization of **1** confirmed the suitability of this dye to serve as a sensitizer for regenerative DSCs on mesoscopic titania films. Device photovoltaic performances were assessed by measuring external quantum efficiencies as a function of wavelength, and current-voltage curves, the latter under simulated AM1.5G one-sun illumination. Varying the concentration of LiI in the redox electrolyte affects the short-circuit photocurrent (J_{SC}), open-circuit voltage (V_{OC}), fill factor (ff), power conversion efficiency (η), and external quantum efficiency (EQE) of the individual devices. Increasing the concentration of LiI results in enormous increases in J_{SC} in the Os(II)-based devices accompanied by corresponding decreases in V_{OC} . Independently increasing the concentration of I^- by using either tetrabutylammonium iodide (TBAI) or the ionic liquid 1-*n*-propyl-3-methylimidazolium iodide (PMII) was found to increase J_{SC} without concomitantly lowering the V_{OC} . These observations are discussed and directly compared in parallel to devices based on the benchmark sensitizer **N3**, *cis*-Ru(dcbpyH₂)₂(NCS)₂. The combined results suggest that the photovoltaic performance of Os(II)-based DSCs can indeed be optimized by simply modifying the composition of redox electrolytes used in the operational sandwich cells. An abundance of I^- appears to be crucial for the effective regeneration of oxidized surface-bound osmium sensitizers and therefore for the production of higher photocurrents in these devices. We note that select devices based on **1** represent the record power conversion efficiency for an Os(II)-based DSC measured under simulated AM1.5G one-sun illumination, $\eta = 4.7\%$.

Triplet Sensitized Red-to-Blue Photon Upconversion. Singh-Rachford, T.N.; Castellano, F.N. *J. Phys. Chem. Lett.* **2010**, 1, 195-200.



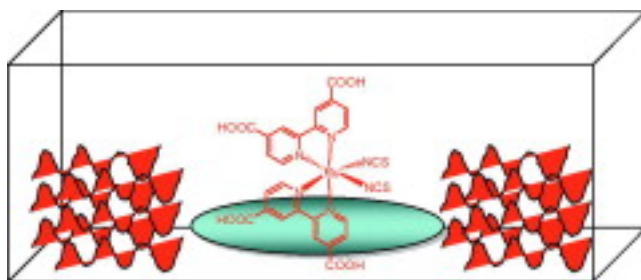
Sensitized red-to-blue upconversion with a record 0.8 eV anti-Stokes shift has been achieved utilizing platinum(II) tetraphenyltetrabenzoporphyrin (PtTPBP) as the triplet sensitizer and perylene as the energy acceptor/annihilator in deaerated benzene. Selective 635 nm excitation of PtTPBP results in the observation of perylene fluorescence centered at 451 nm. Stern–Volmer analysis of dynamic phosphorescence quenching of PtTPBP by perylene yields a triplet–triplet energy transfer quenching constant of $4.08 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Clear evidence for the subsequent triplet–triplet annihilation of $^3\text{perylene}^*$ was afforded by the quadratic dependence of the integrated perylene fluorescence spectra with respect to incident 635 nm light power. The maximum upconversion quantum yield of perylene fluorescence under our sensitized excitation conditions is 0.0065 ± 0.0001 , as ascertained by relative actinometry. The present chromophore combination was successfully translated into the solid state using a low glass transition temperature polyurethane host polymer, which produced upconverted photons for months when stored under ambient conditions.

Photon Upconversion based on Sensitized Triplet-Triplet Annihilation. Singh-Rachford, T.N.; Castellano, F.N. *Coord. Chem. Rev.* **2010**, 254, 2560-2573.

Photon upconversion, the process wherein light of long wavelength is frequency converted to photons of higher energy, is readily achieved at low incident power through sensitized triplet–triplet annihilation (TTA) in various chromophore combinations spanning the UV to the near-IR. This emerging wavelength-shifting technology truly represents a viable route towards converting low energy terrestrial solar photons into light adequate to drive electron transfer in operational photovoltaics. Generalized molecular design constraints, all operational examples reported to date, and measurement techniques applied to these low power nonlinear processes are reviewed in this contribution. In many instances, direct visualization of this phenomenon is presented in solution and within various polymeric host materials.

Controlled Microwave Synthesis of Ru^{II} Synthons and Chromophores Relevant to Solar Energy Conversion. Sun, Y.; Machala, M.L.; Castellano, F.N. *Inorg. Chim. Acta.* **2010**, 363, 283-287.

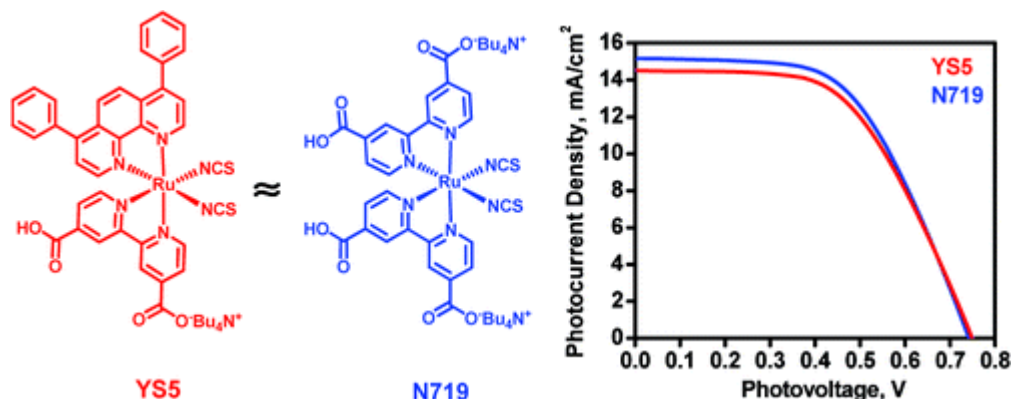
The efficient, high yield atmospheric pressure microwave-assisted synthesis for seven Ru^{II} coordination complexes relevant to solar energy conversion schemes is reported. In all instances, the reaction times have been markedly shortened, concomitant with higher yields with little or no need for subsequent purification and several multi-step reactions proceeded flawlessly in a single pot, including N3, Ru(dcbpy)₂(NCS)₂. In complexes incorporating ester or carboxylic acid functions, open vessel microwave reactions operated at relatively low temperatures maintain the integrity of these groups all the way through the synthesis yielding the desired isolated complexes.



Platinum(II) Acetylide Photophysics. Muro, M.L.; Rachford, A.A.; Wang, X.; Castellano, F.N. *Top. Organomet. Chem.* **2010**, 29, 159-191.

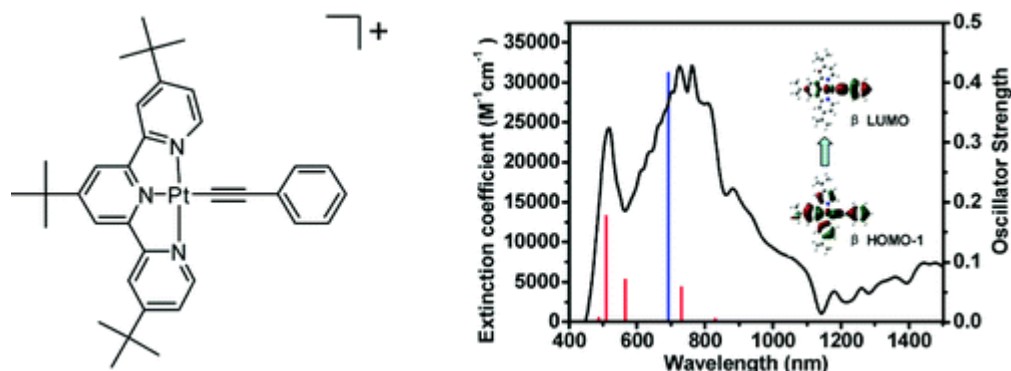
The photophysics of PtII acetylide chromophores represents an important emergent area of research and development. The present review exclusively deals with photophysical processes in square planar PtII complexes of the general formulae: Pt(N[^]N)(C≡CR)₂, [Pt(N[^]N[^]N)(C≡CR)]⁺, Pt(N[^]N[^]C)(C≡CR), *trans*-Pt(PR₃)₂(C≡CR)₂, and *cis*-Pt(P[^]P)(C≡CR)₂, where N[^]N is a bidentate 2,2'-bipyridine, N[^]N[^]N and N[^]N[^]C are tridentate polypyridines, PR₃ is a monodentate phosphine and P[^]P is a bidentate phosphine ligand. These molecules exhibit a range of photophysical attributes depending upon the nature of the lowest electronic triplet excited state(s) which are either charge-transfer, ligand-localized, or an admixture of the two. Under special circumstances, intermolecular interactions further complicate the electronic structures of the ground and excited states and the resulting spectroscopy. Recent computational approaches emphasizing the successful application of DFT and TD-DFT methods towards understanding the absorption and emission processes of these chromophores are also presented.

Viable Alternative to N-719 for Dye-Sensitized Solar Cells. Sun, Y.; Onicha, A.C.; Myahkostupov, M.; Castellano, F.N. *ACS Appl. Mater. Interfaces* **2010**, 2, 2039-2045.



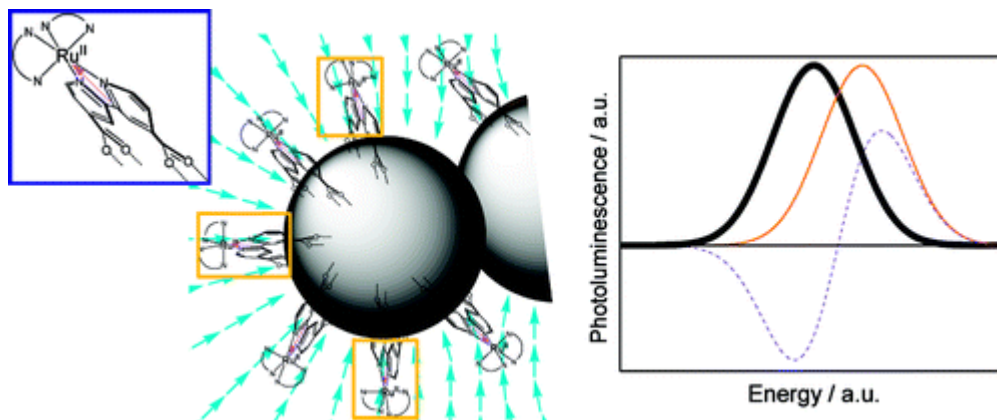
A new synthetically facile heteroleptic ruthenium(II) sensitizer (NBu₄)[Ru(4,7-dpp)(dcbpyH)(NCS)₂], coded as **YS5**, where NBu₄ is tetrabutylammonium, 4,7-dpp is 4,7-diphenyl-1,10-phenanthroline, and dcbpyH is the singly deprotonated surface anchoring derivative of 4,4'-dicarboxy-2,2'-bipyridine (dcbpyH₂), was designed, synthesized, and incorporated into regenerative mesoscopic titania-based dye-sensitized solar cells. The sensitizer has characteristic broad, high extinction coefficient MLCT bands spanning the visible spectrum. The compound was fully characterized by 1D and 2D ¹H NMR, MALDI-TOF-MS, UV-vis, photoluminescence, Raman, IR, and electrochemistry. **YS5** exhibits strong visible absorption properties with a molar extinction coefficient of $1.71 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at its 522 nm maximum. In operational liquid junction-based DSSCs under simulated AM 1.5G one-sun excitation (100 mW/cm²), the photovoltaic performance of **YS5** compares almost equally against the current benchmark sensitizer **N719** in side-by-side comparisons, producing a power conversion efficiency of 6.05% with a maximum IPCE of 65% at 540 nm. The data presented in this manuscript strongly suggest that **YS5** is indeed a viable sensitizer for nanocrystalline TiO₂-based DSSCs, seemingly poised for widespread adaptation.

Excited State Absorption Properties of Pt(II) Terpyridyl Complexes Bearing π -Conjugated Arylacetylides. Wang, X.; Goeb, S.; Ji, Z.; Castellano, F.N. *J. Phys. Chem. B* **2010**, 114, 14440-14449. (Wasielowski Festschrift)



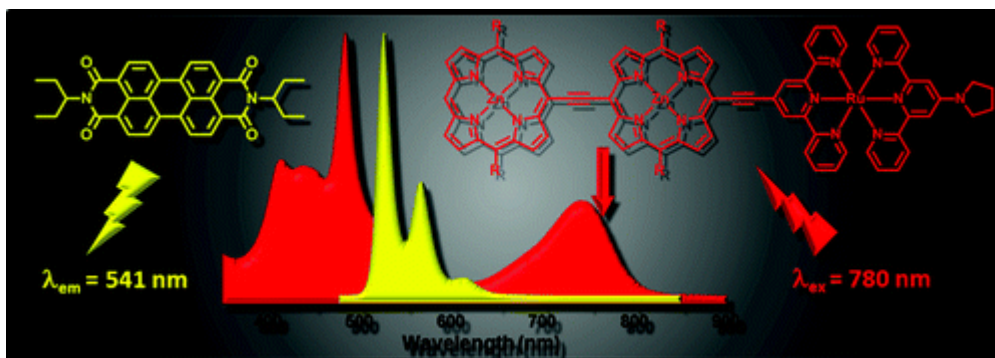
The synthesis, photophysics, and excited state absorption properties of three platinum(II) terpyridyl acetylide charge transfer (CT) complexes possessing a lone ancillary ligand systematically varied in phenylacetylide (PA) π -conjugation length, [Pt(^tBu₃tpy)([C $\equiv$ C-C₆H₄]_n-H)]ClO₄ ($n = 1, 2, 3$), are described. Density functional theory (DFT) calculations performed on the ground states of complexes **1**, **2**, and **3** reveal that their HOMOs reside mainly on the ancillary π -conjugated PA moiety, ranging from 86 to 97%, with LUMOs predominantly centered on the terpyridyl acceptor ligand (91–92%). This electronic structure leads to the production of a triplet ligand-to-ligand CT (³LLCT) excited state upon visible light excitation with minor contributions from the corresponding triplet metal-to-ligand CT (³MLCT) excited state. Unusually strong red-to-near-IR transient absorptions are produced in the excited states of these molecules following selective long wavelength visible excitation of the low energy CT bands that *do not* emanate from the terpyridyl radical anion produced in the CT excited state or from an arylacetylide-based triplet intraligand (³IL) excited state. The extinction coefficients of these low energy absorption transients were determined using the energy transfer method with anthracene serving as the triplet acceptor. A detailed theoretical investigation using DFT and TDDFT methods reveals that these intense near-IR transient absorptions involve transitions resulting from transient oxidation of the PA subunit. In essence, the production of the ³LLCT excited state transiently oxidizes the PA moiety by one electron, producing the corresponding highly absorbing radical cation-like species, analogous to that experienced in related intramolecular photoinduced electron transfer reactions. The computational work successfully predicts the oscillator strength and peak wavelength of the measured excited state absorption transients across this series of molecules. In the present effort, there is a convergence of theory and experiment given that the excited state absorption properties of these Pt(II) chromophores are determined by localized transitions that resemble open shell radical cation species.

Excited-State Electron Transfer from Ruthenium Polypyridyl Compounds to Anatase TiO₂ Nanocrystallites: Evidence for a Stark Effect. Ardo, S.; Sun, Y.; Castellano, F.N.; Meyer, G.J. *J. Phys. Chem. B* **2010**, 114, 14596-14604. (Wasielowski Festschrift)



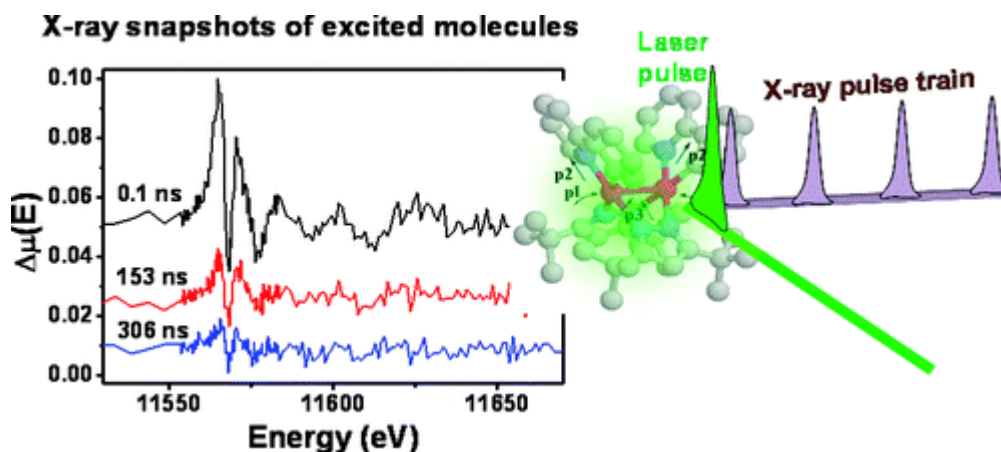
Photophysical studies were performed with [Ru(dtb)₂(dcb)](PF₆)₂ and *cis*-Ru(dcb)(dnb)(NCS)₂, where dtb is 4,4'-(C(CH₃)₃)₂-2,2'-bipyridine, dcb is 4,4'-(COOH)₂-2,2'-bipyridine, and dnb is 4,4'-(CH₃(CH₂)₈)₂-2,2'-bipyridine, anchored to anatase TiO₂ particles (~ 15 nm in diameter) interconnected in a mesoporous, thin film (~ 10 μ m thick) immersed in Li⁺-containing acetonitrile electrolytes. Pulsed-laser excitation resulted in rapid, nonquantitative excited-state injection into TiO₂ with a rate constant that could not be time-resolved, $k_{inj} > 10^8$ s⁻¹, to yield an interfacial charge-separated state. Return of this state to ground-state products displayed observation-wavelength-dependent kinetics due to charge recombination and a second process. The second process occurred in parallel and was assigned to a transient Stark effect created by the electric field originating from the electrons in TiO₂ on ruthenium sensitizers that had not undergone excited-state injection. The kinetics for this processes were well modeled by a stretched exponential function. The impact of this field on the metal-to-ligand charge transfer excited-state of Ru(dtb)₂(dcb)²⁺ or the oxidized form of *cis*-Ru(dcb)(dnb)(NCS)₂ were also investigated. Unambiguous identification of a Stark effect on the excited-state sensitizers was accomplished through fluence-dependent measurements. The possible influence of the electric field on the oxidized sensitizers was at best speculative. The unique relative orientation of the electric field and sensitizer afforded by the nanocrystal geometry resulted in unidirectional shifts in the absorption and photoluminescence spectra of the Ru(II) coordination compounds. On the basis of the magnitude of the shift, it was estimated that a transient field as large as 2.7 MV/cm was generated upon excited-state injection of electrons in TiO₂ at concentrations relevant to an operational dye-sensitized solar cell.

Supramolecular-Chromophore-Sensitized Near-Infrared-to-Visible Photon Upconversion. Singh-Rachford, T.N.; Nayak, A.; Goeb, S.; Muro-Small, M.L.; Therien, M.J.; Castellano, F.N. *J. Am. Chem. Soc.* **2010**, *132*, 14203-14211.



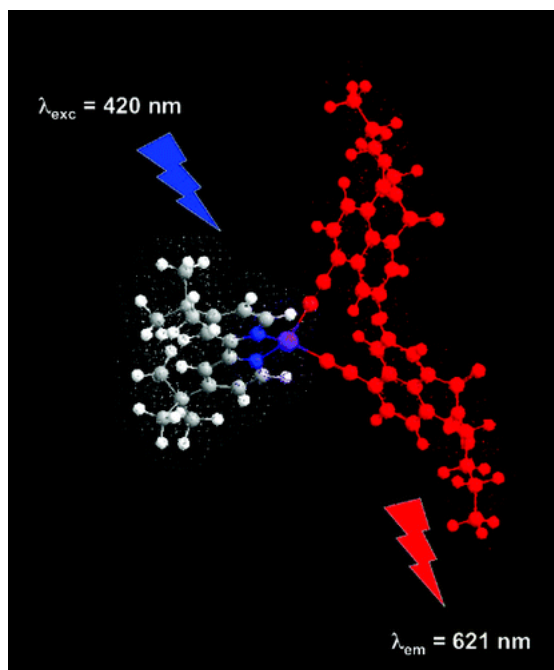
Selective near-IR (NIR) excitation (780 nm) of the conjugated supermolecule ruthenium(II) [15-(4'-ethynyl-(2,2';6',2''-terpyridinyl))-bis[(5,5',-10,20-di(2',6'-bis(3,3-dimethylbutoxy)phenyl)porphyrinato)zinc(II)]ethyne][4'-pyrrolidin-1-yl-2,2';6',2''-terpyridine] bis(hexafluorophosphate) (**Pyr₁RuPZn₂**) in solutions containing *N,N*-bis(ethylpropyl)perylene-3,4,9,10-tetracarboxylicdiimide (**PDI**) or tetracene gives rise to a substantial anti-Stokes energy gain (**PDI**, 0.70 eV; tetracene, 0.86 eV). Experimental data clearly demonstrate that this upconverted fluorescence signal is produced via **Pyr₁RuPZn₂**-sensitized triplet-triplet annihilation (TTA) photochemistry. The TTA process was confirmed by the quadratic dependence of the integrated **¹PDI*** emission centered at 541 nm derived from 780 nm laser excitation. The $T_1 \rightarrow T_n$ excited state absorption decay of **Pyr₁RuPZn₂**, monitored at 900 nm as a function of **PDI** concentration, revealed Stern-Volmer and bimolecular quenching constants of $10\,048\text{ M}^{-1}$ and $5.9 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$, respectively, for the **PDI** triplet sensitization process. The $T_1 \rightarrow T_n$ **PDI** extinction coefficient at 560 nm ($\epsilon_T = 6.6 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$) was determined through the triplet energy transfer method utilizing anthracene as the donor chromophore. **³PDI*** transient triplet absorption dynamics observed as a function of 485 nm incident nanosecond pump laser fluence demonstrate a bimolecular **³PDI***-**³PDI*** TTA rate constant ($k_{TT} = 1.0 \pm 0.2 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$). The maximum quantum yield of the supermolecule-sensitized **PDI** upconverted emission ($\Phi_{UC} = 0.0075 \pm 0.0002$) was determined relative to [Os(phen)₃][PF₆]₂ at an incident laser power of 22 mW at 780 nm. This study successfully demonstrates NIR-to-visible photon upconversion and achieves a new record anti-Stokes shift of 0.86 eV for sensitized TTA, using the supermolecular **Pyr₁RuPZn₂** sensitizer. The stability of the **Pyr₁RuPZn₂/PDI** chromophore combination is readily apparent as continuous irradiation at 780 nm produces 541 nm centered fluorescence with no significant decrease in intensity measured over time domains exceeding several hours. The molecular components of these NIR-to-vis upconverting compositions illustrate that substantial anti-Stokes energy gains via a TTA process can be effortlessly realized.

Triplet Excited State Distortions in a Pyrazolate Bridged Platinum Dimer Measured by X-ray Transient Absorption Spectroscopy. Lockard, J.V.; Rachford, A.A.; Smolentsev, G.; Strickrath, A.; Wang, X.; Zhang, X.; Atenkoffer, K.; Jennings, G.; Soldatov, A.; Rheingold, A.L.; Castellano, F.N.; Chen, L.X. *J. Phys. Chem. A* **2010**, *114*, 12780-12787.



The excited-state structure of a dinuclear platinum(II) complex with *tert*-butyl substituted pyrazolate bridging units, $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})]_2$ (ppy = 2-phenylpyridine; $^t\text{Bu}_2\text{pz}$ = 3,5-di-*tert*-butylpyrazolate) is studied by X-ray transient absorption (XTA) spectroscopy to reveal the transient electronic and nuclear geometry. DFT calculations predict that the lowest energy triplet excited state, assigned to a metal-metal-to-ligand charge transfer (MMLCT) transition, has a contraction in the Pt-Pt distance. The Pt-Pt bond length and other structural parameters extracted from fitting the experimental XTA difference spectra from full multiple scattering (FMS) and multidimensional interpolation calculations indicates a metal-metal distance decrease by approximately 0.2 Å in the triplet excited state. The advantages and challenges of this approach in resolving dynamic transient structures of nonbonding or weak-bonding dinuclear metal complexes in solution are discussed.

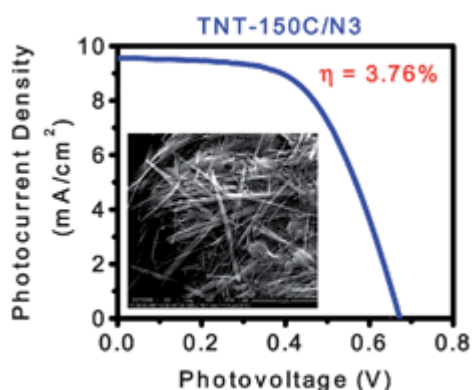
Naphthalimide Phosphorescence Finally Exposed in a Platinum(II) Diimine Complex. Guo, H.; Muro-Small, M.L.; Ji, S.; Zhao, J.; Castellano, F.N. *Inorg. Chem.* **2010**, 49, 6802-6804.



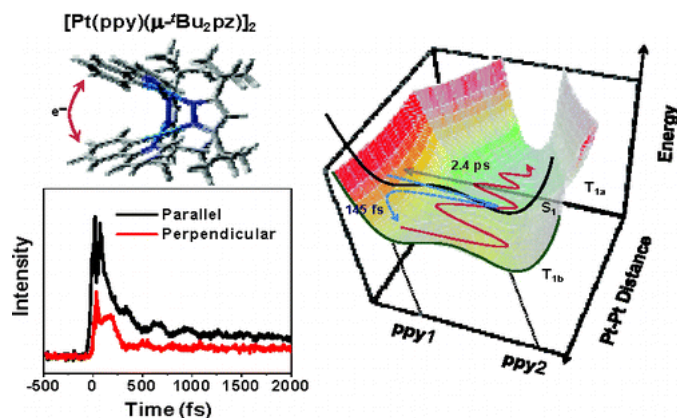
Room temperature (RT) phosphorescence is observed from a naphthalimide species for the first time in the square-planar chromophore $\text{Pt}(\text{dbbpy})(\text{C}\equiv\text{C}-\text{NI})_2$, where NI = *N*-butyl-4-ethynynaphthalimide and dbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine. The combination of static and time-resolved absorption and photoluminescence data is uniformly consistent with triplet-state photophysics localized on an appended $\text{C}\equiv\text{C}-\text{NI}$ unit following excitation into the low-energy absorption bands. This molecule features rather impressive long-lifetime, high-quantum-efficiency NI-based RT phosphorescence ($\tau = 124 \mu\text{s}$; $\Phi = 0.215$) centered at 621 nm, exemplifying how the platinum acetylide linkage strongly promotes intersystem crossing in the NI subunit, representative of a class of molecules whose excited states are typically dominated by singlet fluorescence.

Dye-Sensitized Photovoltaic Properties of Hydrothermally Prepared TiO₂ Nanotubes. Myahkostupov, M.; Zamkov, M.; Castellano, F.N. *Energy Environ. Sci.* **2011**, 4, 998-1010.

Hydrothermal synthesis utilizing aqueous alkaline reaction conditions was employed for the preparation of TiO₂ nanotubes. The ultimate material morphology was found to be extremely sensitive to the nature of the reaction conditions including the chemical nature of the reactor itself—well-defined TiO₂ nanotubes were obtained only when the reaction was carried out in a Teflon reactor/autoclave assembly, as ascertained by electron microscopy imaging. In addition, it was shown that the nanomaterial morphology heavily impacted the performance of dye-sensitized photovoltaic devices based on these materials; devices assembled from well-defined TiO₂ nanotubes exhibited marked overall improvement in the power conversion efficiency. Several individual experimental parameters including hydrothermal synthesis temperature, film thickness, TiO₂ paste composition, and sintering temperature were shown to affect the photovoltaic properties of the resultant solar cells. Upon sensitization with Ru(dcbpyH₂)₂(NCS)₂, optimized devices showed an average power conversion efficiency of $3.76 \pm 0.25\%$ under AM1.5G one sun illumination, seemingly limited by low dye surface coverages.



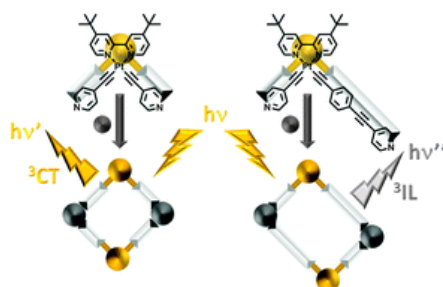
Coherence in Metal-Metal-to-Ligand-Charge-Transfer Transitions of a Dimetallic Complex Revealed by Ultrafast Transient Absorption Anisotropy. Cho, S.; Mara, M.W.; Wang, X.; Lockard, J.V.; Rachford, A.A.; Castellano, F.N.; Chen, L.X. *J. Phys. Chem. A* **2011**, *115*, 3990-3996. (Fleming Festschrift)



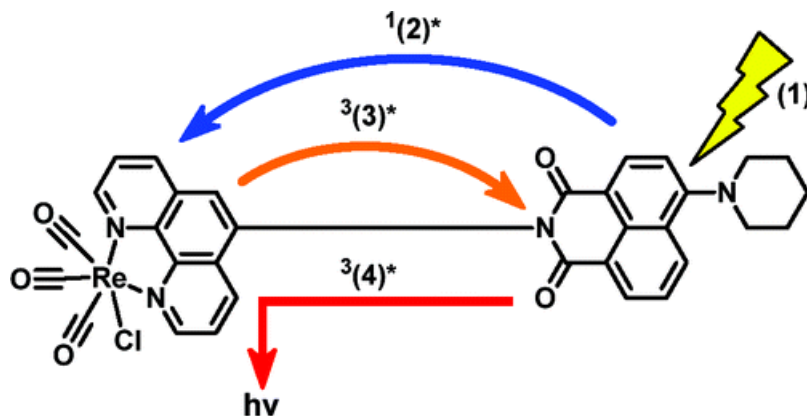
Coherence in the metal-metal-to-ligand-charge transfer (MMLCT) excited state of diplatinum molecule $[\text{Pt}(\text{ppy})(\mu\text{-Bu}_2\text{pz})]_2$ has been investigated through the observed oscillatory features and their corresponding frequencies as well as polarization dependence in the single-wavelength transient absorption (TA) anisotropy signals. Anticorrelated parallel and perpendicular TA signals with respect to the excitation polarization direction were captured, while minimal oscillatory features were observed in the magic angle TA signal. The combined analysis of the experimental results coupled with those previous calculated in the literature maps out a plausible excited state trajectory on the potential energy surface, suggesting that (1) the two energetically close MMLCT excited states due to the symmetry of the molecule may be electronically and coherently coupled with the charge density shifting back and forth between the two phenylpyridine (ppy) ligands, (2) the electronic coupling strength in the $^1\text{MMLCT}$ and $^3\text{MMLCT}$ states may be extracted from the oscillation frequencies of the TA signals to be 160 and 55 cm^{-1} , respectively, (3) a stepwise intersystem crossing cascades follows $^1\text{MMLCT} \rightarrow ^3\text{MMLCT} (T_{1b}) \rightarrow ^3\text{MMLCT} (T_{1a})$, and (4) a possible electronic coherence can be modulated via the Pt-Pt σ -interactions over a picosecond and survive the first step of intersystem crossing. Future experiments are in progress to further investigate the origin of the oscillatory features. These experimental observations may have general implications in design of multimetal center complexes for photoactivated reactions where coherence in the excited states may facilitate directional charge or energy transfer along a certain direction between different parts of a molecule.

Phosphorescent Self-Assembled Pt^{II} Tetranuclear Metallocycles. Goeb, S.; Prusakova, V.; Wang, X.; Vézinat, A.; Sallé, M.; Castellano, F.N. *Chem. Commun.* **2011**, *47*, 4397 - 4399.

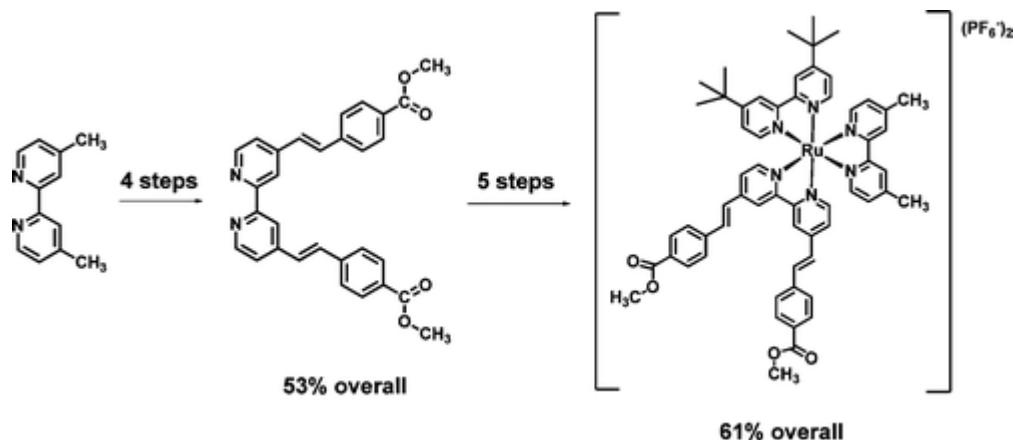
A series of rigid $\text{Pt}(\text{II})$ diimine diacetylide complexes and their corresponding metallocyclic derivatives were synthesized through coordination-driven self-assembly. The photophysical properties of these complexes have been studied in detail, revealing exceptionally high RT phosphorescence quantum yields and lifetimes when the excited state becomes localized on the π -conjugated bridging-ligand following intramolecular charge-transfer sensitization.



Bidirectional "Ping-Pong" Energy Transfer and 3000-Fold Lifetime Enhancement in a Re(I) Charge Transfer Complex. Yarnell, J.E.; Deaton, J.C.; McCusker, C.E.; Castellano, F.N. *Inorg. Chem.* **2011**, 50, 7820-7830.

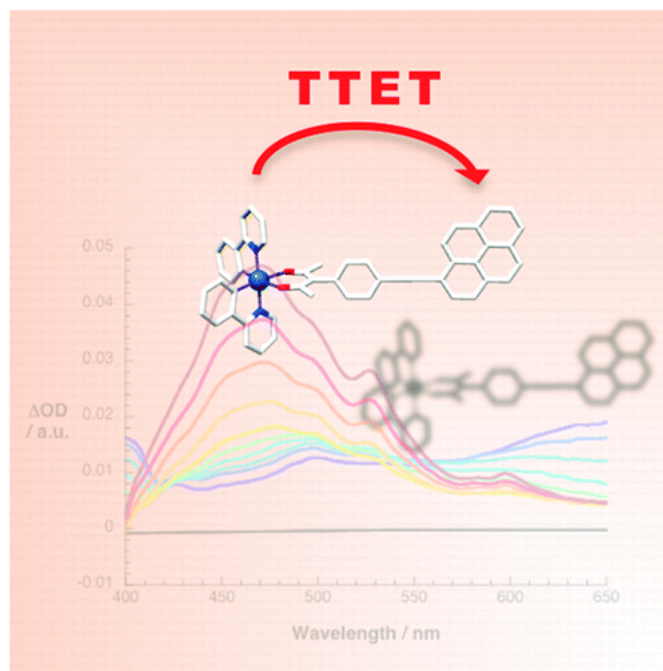


The synthesis and photophysics of a new Re(I)-carbonyl diimine complex, $\text{Re}(\text{PNI-phen})(\text{CO})_3\text{Cl}$, where the PNI-phen is *N*-(1,10-phenanthroline)-4-(1-piperidinyl)naphthalene-1,8-dicarboximide is reported. The metal-to-ligand charge transfer (MLCT) emission lifetime was increased approximately 3000-fold at room temperature with respect to that of the model complex $[\text{Re}(\text{phen})(\text{CO})_3\text{Cl}]$ as a result of thermal equilibrium between the emissive $^3\text{MLCT}$ state and a long-lived triplet ligand-centered (^3LC) state on the PNI chromophore. This represents the longest excited state lifetime ($\tau = 651 \mu\text{s}$) that has ever been observed for a Re(I)-based CT photoluminescence at room temperature. The energy transfer processes and the associated rate constants leading to the establishment of the excited state equilibrium were elucidated by a powerful combination of three techniques (transient visible and infrared (IR) absorption and photoluminescence), each applied from ultrafast to the micro/milliseconds time scale. The MLCT excited state was monitored by transient IR using CO vibrations through time intervals where the corresponding signals obtained in conventional visible transient absorption were completely obscured by overlap with strong transients originating from the pendant PNI chromophore. Following initial excitation of the ^1LC state on the PNI chromophore, energy is transferred to form the MLCT state with a time constant of 45 ps, a value confirmed in all three measurement domains within experimental error. Although transient spectroscopy confirms the production of the $^3\text{MLCT}$ state on ultrafast time scales, Forster resonance energy transfer calculations using the spectral properties of the two chromophores support initial singlet transfer from $^1\text{PNI}^*$ to produce the $^1\text{MLCT}$ state by the agreement with the experimentally observed energy transfer time constant and efficiency. Intersystem crossing from the $^1\text{MLCT}$ to the $^3\text{MLCT}$ excited state is believed to be extremely fast and was not resolved with the current experiments. Finally, triplet energy was transferred from the $^3\text{MLCT}$ to the PNI-centered ^3LC state in less than 15 ns, ultimately achieving equilibrium between the two excited states. Subsequent relaxation to the ground state occurred via emission resulting from thermal population of the $^3\text{MLCT}$ state with a resultant lifetime of 651 μs . The title chromophore represents an interesting example of "ping-pong" energy transfer wherein photon excitation first migrates away from the initially prepared $^1\text{PNI}^*$ excited state and then ultimately returns to this moiety as a long-lived excited triplet which disposes of its energy by equilibrating with the photoluminescent Re(I) MLCT excited state.



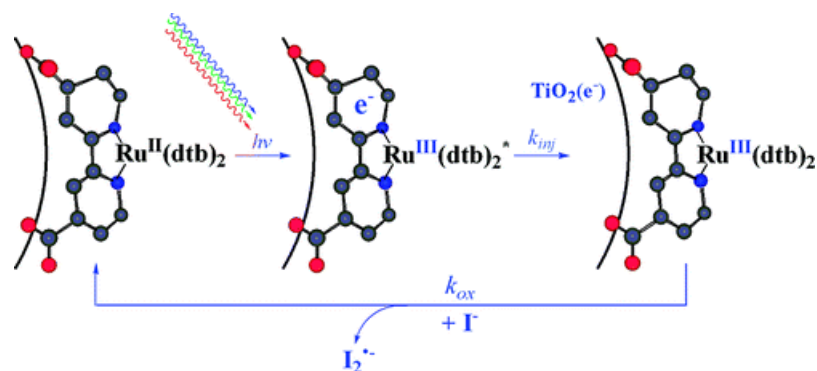
We have developed and optimized a well-controlled and refined methodology for the synthesis of substituted π -conjugated 4,4'-styryl-2,2'-bipyridine ligands and also adapted the tris(heteroleptic) synthetic approach developed by Mann and co-workers to produce two new representative Ru(II)-based complexes bearing the metal oxide surface-anchoring precursor 4,4'-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2'-bipyridine. The two targeted Ru(II) complexes, (4,4'-dimethyl-2,2'-bipyridine)(4,4'-di-*tert*-butyl-2,2'-bipyridine)(4,4'-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2'-bipyridine) ruthenium(II) hexafluorophosphate, [Ru(dmbpy)(dtbbpy)(*p*-COOMe-styryl-bpy)](PF₆)₂ (**1**) and (4,4'-dimethyl-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(4,4'-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2'-bipyridine) ruthenium(II) hexafluorophosphate, [Ru(dmbpy)(dnbpy)(*p*-COOMe-styryl-bpy)](PF₆)₂ (**2**) were obtained as analytically pure compounds in high overall yields (>50% after 5 steps) and were isolated without significant purification effort. In these tris(heteroleptic) molecules, NMR-based structural characterization became nontrivial as the coordinated ligand sets each sense profoundly distinct magnetic environments greatly complicating traditional 1D spectra. However, rational two-dimensional approaches based on both homo- and heteronuclear couplings were readily applied to these structures producing quite definitive analytical characterization and the associated methodology is described in detail. Preliminary photoluminescence and photochemical characterization of **1** and **2** strongly suggests that both molecules are energetically and kinetically suitable to serve as sensitizers in energy-relevant applications.

Excited State Properties of Heteroleptic Ir(III) Complexes bearing Aromatic Hydrocarbons with Extended Cores. Spänig, F.; Olivier, J.-H.; Prusakova, V.; Retailleau, P.; Ziessel, R.; Castellano, F.N. *Inorg. Chem.* **2011**, *50*, 10859-10871.



The synthesis, complete structural characterization, electrochemistry, and excited-state dynamics of a series of four bis-heteroleptic iridium(III) charge-transfer complexes composed of a single acac-functionalized and two ortho-metalated 2-phenylpyridine ligands. The formed iodophenyl complex (**2**) was used as a metallosynthon to introduce extended-core ethynyltolyl (**3**), ethynylpyrene (**4**), and ethynylperylene (**5**) residues into these structures projecting from the acac ancillary ligand. Static and dynamic photoluminescence along with ultrafast and conventional transient absorption measurements in conjunction with cyclic voltammetry were employed to elucidate the nature of the intramolecular energy-transfer processes occurring in the excited states of polychromophores **4** and **5** and are directly compared with those of model complexes **2** and **3**. Upon charge-transfer excitation of these molecules, the long-lived triplet-state metal-to-ligand charge-transfer ($^3\text{MLCT}$)-based photoluminescence readily observed in **2** and **3** ($\tau = 1 \mu\text{s}$) is nearly quantitatively quenched, resulting from production of the associated triplet intraligand (^3IL) excited states in **4** and **5** through intramolecular triplet-triplet energy transfer. The respective formation of the extended-core $^3\text{pyrenyl}$ and $^3\text{perylene}$ -localized excited states in **4** and **5** is confirmed by their ultrafast excited-state evolution, which ultimately generates features associated with these ^3IL excited states and their greatly extended excited-state lifetimes with respect to the parent complexes **2** and **3**.

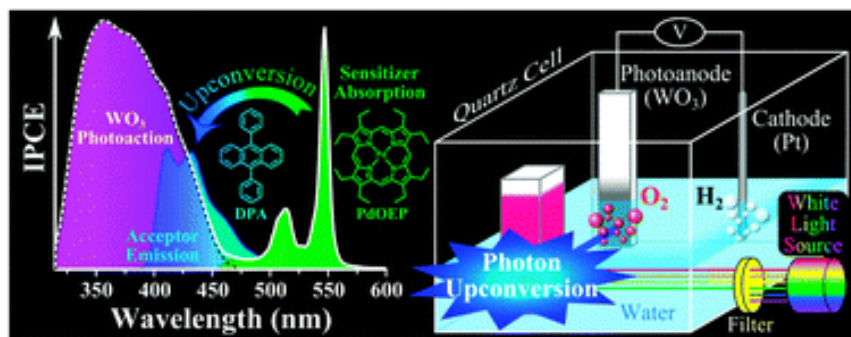
Charge Recombination to Oxidized Iodide in Dye-Sensitized Solar Cells. Rowley, J.; Ardo, S.; Sun, Y.; Castellano, F.N.; Meyer, G.J. *J. Phys. Chem. C* **2011**, *115*, 20316-20325.



The goal of this study was to determine whether electrons injected into TiO_2 in dye-sensitized solar cells (DSSCs) react with di-iodide, I_2^- , a known intermediate in sensitized iodide oxidation. The approach was to utilize time-resolved absorption spectroscopy to quantify the yield of I_2^- disproportionation under conditions where I_2^- reduction by electrons photoinjected into TiO_2 , $\text{TiO}_2(\text{e}^-)$ s, could be competitive. The DSSC was based on $[\text{Ru}(\text{dtb})_2(\text{dcb})]^{2+}$, where dtb is 4,4'-($\text{C}(\text{CH}_3)_3$)₂-2,2'-bipyridine and dcb is 4,4'-(COOH)₂-2,2'-bipyridine, sensitized mesoporous nanocrystalline TiO_2 thin films sintered onto an optically transparent fluorine-doped tin oxide (FTO) conductive substrate. A transparent Pt counter-electrode and a 0.5 M LiI/0.05 M I_2 /acetonitrile electrolyte completed the DSSC. After pulsed 532 nm laser excitation, the first iodide oxidation product observed spectroscopically was I_2^- . Under all conditions studied, there was no direct evidence for the reaction between $\text{TiO}_2(\text{e}^-)$ and I_2^- , and the kinetics for I_2^- loss indicated quantitative disproportionation of I_2^- to yield I_3^- and I^- with a rate constant that was, within experimental error, the same as that measured in fluid acetonitrile solution, $2.2 \pm 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This was true even when steady state illumination was utilized to increase the $\text{TiO}_2(\text{e}^-)$ concentration. Data consistent with charge recombination to I_3^- , from $\text{TiO}_2(\text{e}^-)$ or electrons at the Pt counter electrode, were quantified spectroscopically, with the Kohlrausch–Williams–Watts (KWW) function, at specific points on the current–potential curve. This reaction was found to be sensitive to steady state illumination incident on the DSSC. Transient absorption changes assigned to a Stark effect that were intimately coupled to the presence of transiently generated $\text{TiO}_2(\text{e}^-)$ complicated charge recombination analysis.

Upconversion-Powered Photoelectrochemistry. Khnayzer, R.S.; Blumhoff, J.; Harrington, J.A.; Deng, F.; Haefele, A.; Castellano, F.N. *Chem. Commun.* **2012**, *48*, 209-211.

Upconversion photochemistry occurring between palladium(II) octaethylporphyrin (PdOEP, 1) and 9,10-diphenylanthracene (DPA, 2) in toluene successfully sensitizes nanostructured WO_3 photoanodes ($E_g = 2.7 \text{ eV}$) to sub-bandgap non-coherent green photons at low power density.



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