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ARTICLE

MLCT Sensitizers in Photochemical Upconversion: Past, Present, and Potential Future Directions

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This treatment highlights the historical development of MLCT sensitizers in photochemical upconversion while indentifying current state-of-the-art and exciting opportunities in this arena moving towards the future.

Introduction

Although the concept of photochemical upconversion through sensitized triplet fusion (Fig. 1) originated in the early 1960's,[1] it was not until 2004 where metal-to-ligand charge transfer (MLCT) chromophores were first employed.[2] Immediately, it became clear that MLCT triplet sensitizers coupled with aromatic hydrocarbon emitters readily accomplished anti-Stokes wavelength shifting in a trivial manner. This initial work laid the foundation from which emerged a rather immense worldwide scientific effort exploring various aspects of this important technology. Since there are ample recent reviews highlighting both fundamental and applied aspects of sensitized triplet fusion,[3-6] further discussion here is unwarranted. As such, the focus of this treatment concerns

only MLCT photosensitization of triplet-triplet annihilation (TTA), a subfield of photochemical upconversion well positioned for more extensive investigation. MLCT excited states provide the opportunity for systematic variation of absorption and photophysical properties from structurally related sensitizers. Photochemical upconversion efficiencies and anti-Stokes emission properties rely on numerous factors including triplet sensitizer extinction coefficient, excited state lifetime and energy, as well as photostability. Therefore, MLCT chromophores have much to offer in the conception of future frequency shifting molecular compositions and materials functioning through sensitized TTA.
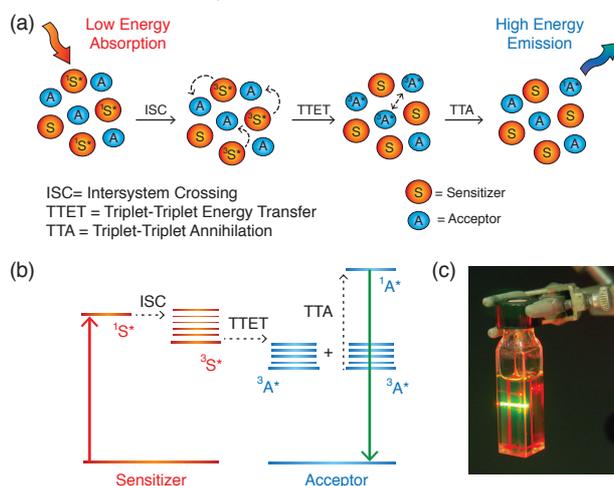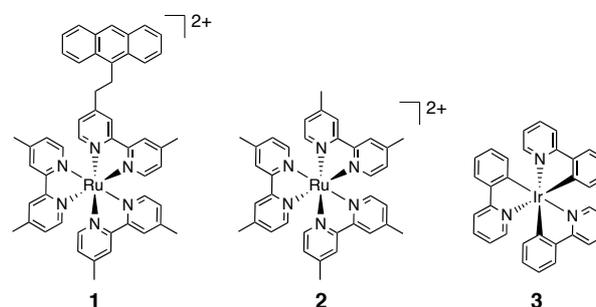

Figure 1. (a) Illustration of the photochemical upconversion process. (b) General Jablonski diagram showing the energy requirements of sensitizer and acceptor species. (c) Digital photograph of red-to-green upconversion sensitized by a Cu(I) complex.

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The Early Years: 2004 - 2008

The utilization of MLCT excited states in sensitized triplet fusion schemes originated with Ru(II) bipyridyl complexes, following the design criteria outlined in Fig. 1. Years of research in this area has illustrated that as long as the energetic criteria of the sensitizer and acceptor/annihilator displayed in Fig. 1 are met, sensitized triplet fusion is likely to occur with efficiencies dominated by the relevant kinetic processes.[4] In essence, the sensitizer singlet and triplet energy levels should be sandwiched between those same levels in the acceptor/annihilator species. In the very first report, long wavelength MLCT excitation of the dyad $[Ru(dmb)_2(bpy-An)]^{2+}$ (**1**) in CH_3CN solution produced upconverted delayed singlet anthracene fluorescence resulting from bimolecular TTA.[2] In

actuality, the spectral overlap for resonance energy transfer between the ^{1}An* emission and the Ru(II) MLCT absorption was so significant that control experiments separating the donor and acceptor produced much higher yields of singlet anthracene fluorescence. This led to a follow up (and more recognized) contribution that exploited the near unity fluorescence quantum yield of 9,10-diphenylanthracene (DPA).[7] Simple mixtures of [Ru(dmb)$_3$]$^{2+}$ (**2**) and DPA generated such strong upconverted emission that it could be easily discerned by the naked eye. Instead of light-producing upconversion, it was also demonstrated that sensitized triplet fusion could be manipulated to generate new chemical bonds. Specifically, [4+4] cycloaddition photochemistry in anthracene was sensitized to visible light using [Ru(dmb)$_3$]$^{2+}$.[8] Also in 2006 it was shown that selective excitation of *fac*-Ir(ppy)$_3$ (**3**) in the visible produced upconverted ultraviolet fluorescence in both pyrene and di-*tert*-butylpyrene.[9] Steric bulk in the latter inhibited excimer formation thereby preserving the anti-Stokes shift. In 2007, sensitizer research was focused primarily on metalated porphyrins and phthalocyanines as their long excited state lifetimes made them valuable for efficient triplet sensitization.[3, 10-12] A lone contribution in 2008 related to MLCT sensitized upconversion of 9,10-dimethylanthracene (DMA) and featured the concept of monochromatic (514.5 nm) to broadband white light generation through upconversion with simultaneous DMA excimer downconversion.[13]
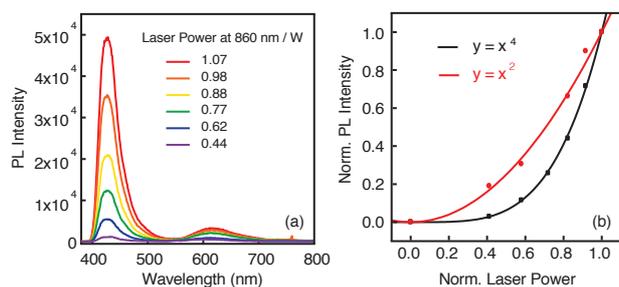

Figure 2. (a) Emission intensity profile of upconverted DPA and residual photoluminescence of [Ru(dmb)$_3$]$^{2+}$ following selective excitation of [Ru(dmb)$_3$]$^{2+}$ at 860 nm in a deaerated CH$_3$CN. (b) Normalized integrated emission intensity of DPA (black) and [Ru(dmb)$_3$]$^{2+}$ (red) from panel (a) plotted as a function of the normalized incident light power. The solid black and red lines represent the best quartic (x^4) and quadratic (x^2) fits to the data points, respectively. Adapted from ref. 14.

## Expansion of MLCT Sensitized Upconversion: 2009 - 2012

In 2009, an interesting incident light dependence phenomenon was reported that combined triplet-triplet annihilation photochemistry with simultaneous two-photon excitation.[14] A mixture of [Ru(dmb)$_3$]$^{2+}$ and DPA excited with focused 860 nm laser pulses from a Ti-Sapphire oscillator produced singlet DPA fluorescence exhibiting a quartic (x^4) four-photon incident light power dependence with a concomitant 1.38 eV anti-Stokes shift for sensitized TTA (Fig. 2). In essence, two-photon excitation occurs in two separate sensitizers, producing two ^{3}DPA* chromophores that ultimately annihilate with this unusual quartic incident light power dependence. Although

this remains the only report of such a phenomenon, this approach may be valuable for imaging applications in the future. From this point forward, the field experienced a rapid expansion over the next several years. In 2010, the realm of charge transfer sensitizers was expanded to include Pt(II) terpyridylacetylides,[15] whose energetics are similar to many of the previous investigated Ru(II) excited states. A multichromophoric dendrimer containing a Ru(II) MLCT core and 4 peripherial DPA subunits for energy upconversion was also developed.[16] Expanding on lifetime extension themes developed for MLCT excited states,[17] a series of papers were published in 2011 and 2012 focused on enhancing sensitizer lifetimes, making them more susceptible to bimolecular triplet energy transfer chemistry.[18-25] Specifically, Ru(II), Ir(III), and Pt(II) complexes bearing long-lived triplet intraligand (^{3}IL) excited states were all shown to sensitize upconversion in numerous organic triplet acceptor chromophores.
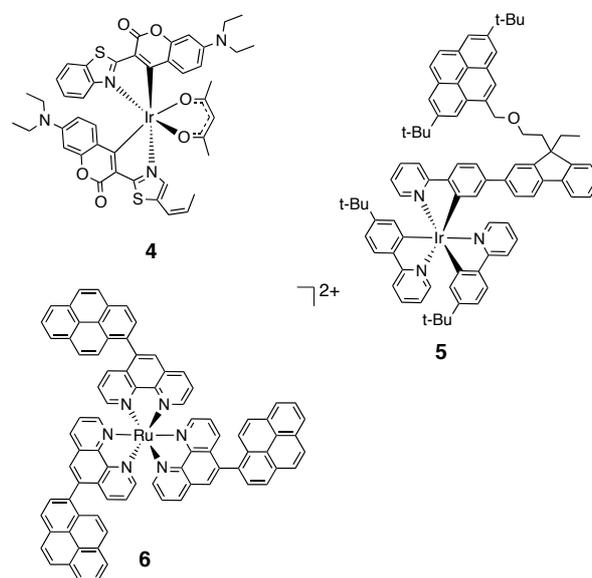
Current State-of-the-Art: 2013 – 2015

Work has continued to develop lifetime extended Ir(III) and Pt(II)-based sensitizers for upconversion schemes.[26-28] Meanwhile, additional research groups have come onto the scene with new ideas involving sensitizers and acceptors/annihilators. For example, workers in Japan recently developed a benchmark Ir(III) sensitizer (**4**) for low power visible-to-UV upconversion.[29] In related work, a series of donor-acceptor Ir(III)/pyrenyl chromophores (**5**) were prepared featuring upconversion reminiscent of the original dyad motif **1**.[30] Upconverting polymers featuring Ru(II) and DPA subunits have also been recently investigated for potential solid-state applications.[31, 32] Over this same time frame, a lifetime extended Ru(II) chromophore (**6**) developed many years ago was successfully applied to photochemical upconversion.[33] An undergraduate laboratory experience based on one of the original Ru(II)/anthracene upconversion compositions has also been developed.[34] A common theme
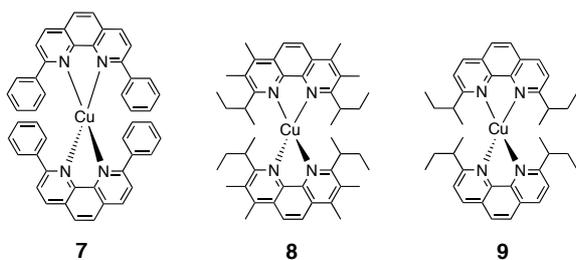
emerges from all of the work described above, namely, all of the MLCT sensitizers contain expensive and rare late transition metal cations. In 2013, questions started to emerge as to whether viable alternative charge transfer sensitizers could be identified and successfully applied in upconversion schemes.

The original proof-of-concept experiments highlighted the use of [Cu(dpp)$_2$]$^+$ (**7**) as sensitizer in conjunction with perylene and the laser dye pyrromethene 546 as emitters.[35] These compositions afforded orange-to-blue and red-to-green wavelength conversions, respectively. The main limitation with using [Cu(dpp)$_2$]$^+$ as a sensitizer resided in its short excited state lifetime that greatly inhibited the triplet sensitization chemistry forcing the use of large chromophore concentrations. This problem was circumvented in 2015 by applying recently developed long-lifetime Cu(I) sensitizers,[36] [Cu(dsbtmp)$_2$]$^+$ (**8**) and [Cu(dsbp)$_2$]$^+$ (**9**) to photochemical upconversion.[37] These molecules were paired with anthracene, DMA, and DPA to afford visible to near-UV upconversion in all instances (Fig. 3). In the case of **8**, the measured upconversion quantum yields with DMA (9.2%) and DPA (17.8%) exceed the upconversion quantum yield values sensitized by Ru(II) polypyridyl chromophores.
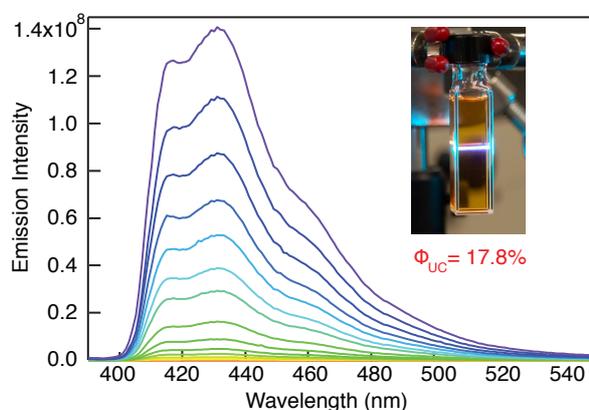

Figure 3. Upconverted emission spectra of DPA sensitized by **8** in deaerated dichloromethane solution with 488 nm excitation. Inset is the digital photograph of the upconversion solution under 488 nm irradiation. Adapted from ref. 37.

Future Outlook

To date, all of the MLCT sensitized upconversion work has been accomplished with a limited number of photosensitizers, namely Ru(II) polypyridyl, cyclometalated Ir(III), Pt(II) polyimine acetylide, and Cu(I) *bis*-phenanthroline complexes. With the incredible diversity of MLCT chromophores established in the literature, there are many other classes of molecules that meet the requirements necessary to sensitize

photon upconversion. In particular, recent work leveraging Cu(I) sensitizers provide an impetus to the community to search for other viable first row candidates. The resurgence of zero valent d^6 MLCT excited states suggest that early transition metal complexes may possibly emerge as viable candidates.[38] The acceptor/annihilator selections to date have been extremely limited and can be considered largely unexplored. With few exceptions, the vast majority of acceptors/annihilators used in MLCT sensitized photochemical upconversion (and in the area of photochemical upconversion as a whole) are aromatic hydrocarbons including anthracene, rubrene, perylene, and pyrene derivatives. New classes of annihilators, with high quantum yield fluorescence ranging from the UV to the red and near-IR, would markedly expand the scope of available wavelength conversions. Similarly, the notion of using multiple triplet acceptors, where one quenches the sensitizer and transmits the triplet energy to a second acceptor poised for annihilation, represents another area poised for immediate exploration.[39] The continued development of photonic polymers in upconversion[40, 41] also shows promise for the integration of MLCT sensitizers in future research endeavors.

Acknowledgements

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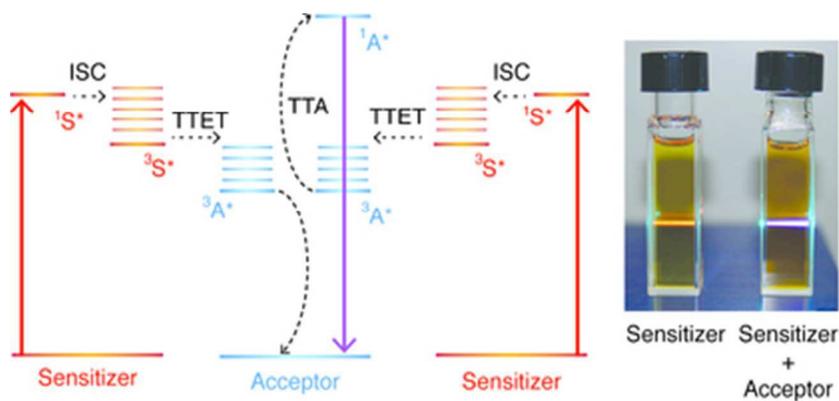
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