Upconverted Emission from Pyrene and Di-*tert*-butylpyrene Using Ir(ppy)$_3$ as Triplet Sensitizer

Wei Zhao and Felix N. Castellano*

Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

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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.

Introduction

The widespread availability of high peak power pulsed lasers has spawned intensive investigations regarding the fundamental and applied aspects of simultaneous two-photon absorption processes.[1−9] One intriguing facet of simultaneous two-photon absorption is that low-energy photons are used to produce higher energy excited states. Although significant contributions have been made in this area in recent history,[1−9] the fact remains that two-photon absorption processes necessitate the use of expensive pulsed lasers to afford sample excitation. A plausible and economic alternative to this strategy would harness sequential highly allowed one-photon absorptions to create higher energy excited states. One approach is to take advantage of triplet−triplet annihilation (TTA) reactions where the energy stored in two separate excited triplet molecules are combined to generate a higher energy excited singlet state and a corresponding ground-state species.[10−12] To observe upconversion in this scenario, the annihilating triplets must be sensitized using photons of significantly longer wavelength than those required to afford direct excitation of the singlet state. This strategy was first explored by Parker and Hatchard in noncovalent organic systems where the mechanism of sensitized TTA yielded upconverted fluorescence.[10] More recently, our group[13−15] and others[16] have applied this concept toward the goal of low-power upconversion, where sequential one-photon absorptions are used to produce higher energy excited states. The advantage of this approach lies in the fact that low-power continuous-wave light sources can be used as the excitation source to drive these intrinsically nonlinear processes.

For example, we have reported that the judicious selection of an appropriate metal-to-ligand charge-transfer (MLCT) sensitizer in concert with an aromatic hydrocarbon energy acceptor can lead to efficient photon upconversion. Selective excitation of the MLCT transition in $[\mathrm{Ru(dmb)_3}]^{2+}$ (dmb = 4,4′-dimethyl-2′2-bipyridine) in the presence of anthracene or 9,10-diphenylanthracence yields easily visualized upconverted singlet fluorescence resulting from triplet−triplet annihilation at low excitation power.[14] The feasibility of efficient photochemically driven upconversion processes using Ru$^{\mathrm{II}}$ metal complex triplet sensitizers has been clearly demonstrated, and the pertinent bimolecular triplet quenching (eq 1) and triplet−triplet annihilation reactions (eq 2) are given below:

$$[\mathrm{Ru(dmb)_3}]^{2+*} + \mathrm{An} \rightarrow [\mathrm{Ru(dmb)_3}]^{2+} + {}^3\mathrm{An}^* \qquad (1)$$

$${}^3\mathrm{An}^* + {}^3\mathrm{An}^* \rightarrow {}^1\mathrm{An}^* + \mathrm{An} \qquad (2)$$

The energetics of this reaction sequence mandate that the singlet and triplet states of the metal complex sensitizer be nested between the singlet and triplets of the aromatic hydrocarbon energy transfer acceptor/annihilator.[10] As long as these energetic criteria are met and the final acceptor has the ability to triplet−triplet annihilate, then upconverted emission can be anticipated from a mixture of appropriate chromophores. Triplet annihilation reactions produce excited singlet states with substantial excess energy (2 × T_1), and therefore higher energy singlet states may be accessed using this approach. Also, sensitized TTA reactions also have synthetic utility as we have recently demonstrated the process of photochemical upconversion, where the prototypical anthracene dimerization reaction was afforded through selective visible excitation of a Ru(II) chromophore.[15]

Importantly, there are many different known metal complexes based on Ir(III) which possess long-lived excited states that can potentially serve as "high-energy" triplet sensitizers for the

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* To whom correspondence should be addressed. Phone: (419) 372-7513; fax: (419) 372-9809; e-mail: castell@bgsu.edu.

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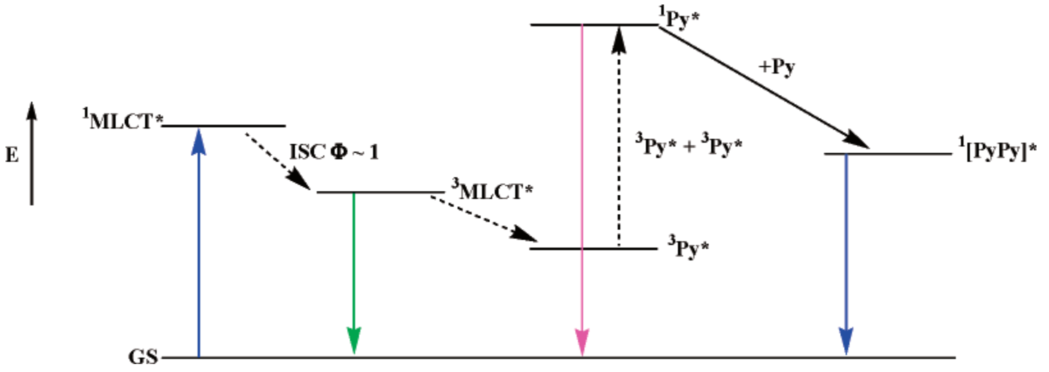
SCHEME 1: Qualitative Energy Level Diagram of the Upconversion Process Associated with Ir(ppy)$_3$ Triplet State Sensitization of Pyrene Leading to Singlet Pyrene and Pyrene Singlet Excimer Fluorescence[a]



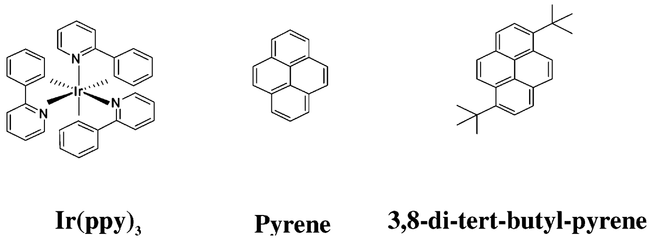
[a] The solid colored lines represent radiative processes.

production of short wavelength (UV) upconverted photons. Moreover, these complexes have absorption bands that tail into the visible region, permitting their selective excitation with low-energy sources. If combined with the appropriate acceptor molecules, upconverted fluorescence would be expected. In essence, one approach to create high-energy emission via upconversion will require the use of inorganic sensitizers with large triplet state energies and triplet acceptors with higher singlet/triplet levels. Since our work to date has only utilized Ru(II) complexes in conjunction with anthracene and diphenylanthracene,[13−15] the present study was initiated to demonstrate that a wider range of inorganic donor/organic acceptor systems are amenable to sensitized TTA processes.

Tris(2-phenylpyridine) iridium(III), Ir(ppy)$_3$, has attracted attention because of its application as the active layer in organic light-emitting diodes (OLEDs).[17] Of particular relevance to the current work, this photostable molecule possesses a high triplet energy (~20 000 cm^{-1}) with a long excited-state lifetime (~1.55 μs).[18] The intersystem crossing in Ir(ppy)$_3$ is rapid and the quantum yield for ^{3}MLCT formation is generally accepted as unity,[19] thus making it a suitable sensitizer for TTA. The familiar aromatic hydrocarbon molecule pyrene has singlet and triplet energies of ~26 100 cm^{-1} and ~16 850 cm^{-1}, respectively,[20] and will serve as the triplet energy transfer acceptor/annihilator in the present study. The ability for singlet excited pyrene to produce excimers[21] in solutions containing large concentrations of ground-state pyrene molecules provides an interesting opportunity to study how sensitized TTA processes influence excimer production. The qualitative energy level diagram presented in Scheme 1 depicts the process of upconversion in the Ir(ppy)$_3$/pyrene system and shows the possible emission-producing reaction paths following selective excitation of Ir(ppy)$_3$. In this particular case, both sensitized upconverted singlet pyrene and singlet pyrene excimer fluorescence can be generated. The utilization of 3,8-di-*tert*-butylpyrene in place of pyrene in the sensitized TTA studies is expected to suppress excimer formation at high acceptor concentrations.

The current work explores sensitized TTA processes using time-resolved photoluminescence methods in conjunction with Ir(ppy)$_3$ and the two pyrene molecules discussed above, Chart 1. Selective pulsed laser excitation of Ir(ppy)$_3$ at 450 nm produces upconverted fluorescence in pyrene in the UV, consistent with the TTA mechanism. At high concentrations of pyrene, the emission from excimers resulting from selective excitation of Ir(ppy)$_3$ becomes quite strong at longer wavelengths, unfortunately degrading the energy stored in the TTA-sensitized singlet excited state. Sensitized excimer production is largely suppressed when 3,8-di-*tert*-butylpyrene is employed as the triplet acceptor/annihilator.

CHART 1



Experimental Section

Materials. Pyrene (Aldrich, 99%) was purified by passing two times through a silica gel column, followed by recrystallization from hexane. Iridium(III) acetylacetonate (Ir(acac)$_3$), 2-phenylpyridine (Hppy), and *t*-BuCl were obtained from Aldrich and were used as received. All other reagents and solvents from commercial sources were used as received.

Synthesis of Ir(ppy)$_3$. The original authentic sample of Ir(ppy)$_3$ was synthesized using a procedure similar to that in the literature,[22] which requires long reaction times (10 h). In an attempt to shorten the preparation time of the Ir(ppy)$_3$ complex, we adopted a microwave-assisted synthetic method. In a typical reaction, Ir(acac)$_3$ (50 mg) and Hppy (0.09 mL) were dissolved in degassed glycerol (5 mL) and were subjected to microwave (Discover, CEM Corporation) irradiation which maintained the reaction temperature at 207 °C for 10 min. One molar HCl (30 mL) was added to the brown solution after cooling, and the product precipitated. The solid was collected by filtration through a fine glass frit. For further purification, the product was dissolved in hot dichloromethane and was passed through a silica gel column to remove dark colored impurities. After evaporating the dichloromethane, the yellow powder product was isolated in 16% yield.

Synthesis of 3,8-Di-*tert*-butylpyrene. 3,8-Di-*tert*-butylpyrene was synthesized as outlined in the literature.[23] Briefly, AlCl$_3$ (0.2 g) was added to a solution of pyrene (10 g) in *t*-BuCl (12 g). After stirring for 1 h, additional AlCl$_3$ (0.8 g) was added to the mixture which was permitted to stand overnight. The reaction mixture was then heated and maintained at 50 °C for 10 min and finally was quenched with ice-cold dilute HCl. The product was dissolved in dichloromethane and was filtered. The filtrate was passed through a silica gel column (33% DCM and 67% hexanes mixture as solvent) which removed some black colored impurities. The collected fractions were rotary evaporated to dryness, and the final solid product was recrystallized from hot CH_3CN.

Photophysical Measurements. Absorption spectra were measured with a Hewlett-Packard 8453 diode array spectrophotometer, accurate to ±2 nm. Static luminescence spectra were obtained with a single-photon-counting spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 900). The excitation was accomplished with a 450 W Xe lamp optically coupled to a monochromator (±2 nm), and the emission was gathered at 90° and was passed through a second monochromator (±2 nm). The luminescence was measured with a Peltier-cooled (−30 °C), R955 red sensitive photomultiplier. Excitation spectra are corrected with a photodiode mounted inside the fluorimeter that continuously measures the Xe lamp output. Transient emission intensity decays were measured with a nitrogen-pumped broad-band dye laser (2−3 nm fwhm) from PTI (GL-3300 N_2 laser, GL-301 dye laser), using an apparatus that has been previously described.[24] Coumarin 460 (440−480 nm) dye was used to tune unfocused excitation. An average of 128 transients was collected, transferred to computer, and processed using Origin 7.5.

Upconverted Fluorescence Experiments. Time-resolved photoluminescence experiments were performed as described previously[13,24] with some minor modifications. All samples were deaerated with argon gas for at least 30 min prior to measurements and were continuously purged throughout the experiments. The 450 ± 2 nm output of the N_2 pumped dye laser was passed through a 430-nm-long pass filter prior to incidence on the sample, and the pulse energy was systematically varied through the use of neutral density filters (Rolyn Optics). The pulse energies were measured at the sample position using a Molectron Joulemeter (J4-05). To obtain signal intensities sufficient for time-resolved spectra with adequate wavelength resolution, the luminescence transients were amplified by terminating the photomultiplier tube (PMT) signal through a 10 kΩ resistor to the oscilloscope (400 MHz). The fluorescence intensities measured with variation in laser power were determined by signal averaging 128 transients at each laser power. The individual transients were integrated over the entire upconverted fluorescence profile yielding relative intensities that were each reproducible within 1% of their respective values.

Results and Discussion

Figure 1 displays the absorption spectra for $Ir(ppy)_3$, pyrene, and *tert*-butylpyrene in CH_2Cl_2. The absorption of $Ir(ppy)_3$ shows an intense band in the range of 250−320 nm, which is due to the singlet−singlet $\pi-\pi^*$ transitions of the ligands. A weaker MLCT absorption band extends from 330 nm and tails into the visible. Both pyrene and *tert*-butylpyrene have maximum singlet absorptions centered at ~340 nm. In the time-resolved photoluminescence experiments, 450 nm was chosen as the excitation wavelength to ensure selective excitation of the metal complex in all instances.

The photoluminescence spectra of $Ir(ppy)_3$, pyrene, and *tert*-butylpyrene in deareated CH_2Cl_2 are displayed in Figure 2. The MLCT emission band of $Ir(ppy)_3$ is centered near 515 nm with quantum yield of 0.61, which is higher than the reported value of 0.50 in toluene.[25] The quantum yields for pyrene in a series of solvents have been previously investigated and reported to be 0.38 in dichloromethane.[26] In the current experiments, the absolute quantum yields of pyrene and *tert*-butylpyrene in CH_2Cl_2 were evaluated relative to quinine sulfate in 0.1 M H_2SO_4 as standard, which has a quantum yield of 0.577 (λ_{ex} = 350 nm).[27] Our results show that the fluorescence quantum yields for pyrene and *tert*-butylpyrene are 0.35 and 0.39, respectively, within experimental error of the values determined previously. The fluorescence spectrum of pyrene at higher concentrations displays monomeric emission between 360 and 420 nm in addition to a new broad featureless band centered at 470 nm which is characteristic of an excimer.[28] It is well established that the pyrene excimer readily forms under conditions which facilitate collisional quenching of an excited pyrene molecule with a corresponding ground-state species. Only the emission from the monomer could be detected in the case of *tert*-butylpyrene at all concentrations studied. The steric bulk afforded by the two tert-butyl substituents successfully blocks the formation of excimers in these molecules.

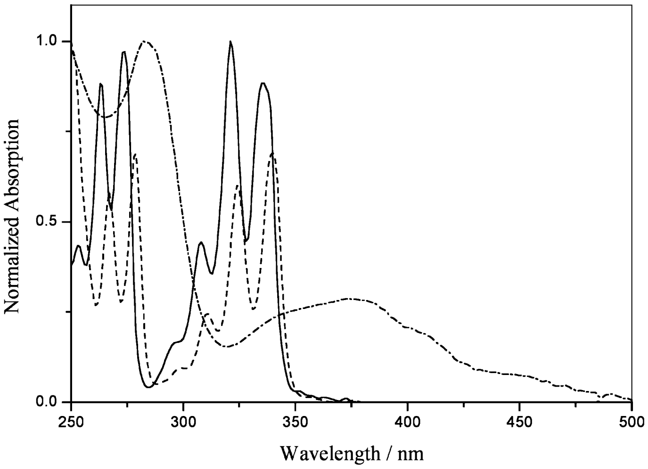


Figure 1. Absorption spectra of $Ir(ppy)_3$ (dash−dot line), pyrene (dotted line), and 3,8-di-*tert*-butylpyrene (solid line) in CH_2Cl_2 at room temperature.

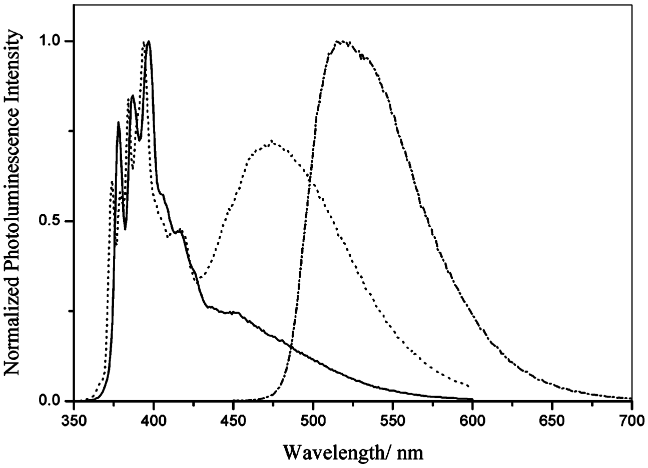


Figure 2. Photoluminescence spectra of $Ir(ppy)_3$ (1×10^{-5} M) excited at 390 nm (dash−dotted line) and pyrene (1×10^{-3} M) (dotted line) and di-*tert*-butyl pyrene (1×10^{-3} M) (solid line) excited at 340 nm. All samples were measured in deaerated CH_2Cl_2.

The MLCT-based photoluminescence in $Ir(ppy)_3$ is efficiently quenched by both pyrene and *tert*-butylpyrene and can be readily quantified by the Stern−Volmer relation (eq 3)

$$I_0/I = \tau_0/\tau = 1 + K_{sv}[Q] \tag{3}$$

where I_0 and I are the photoluminescence intensities and τ_0 and τ are the lifetimes in absence and presence of quencher, respectively; [Q] is the molar concentration of quencher. From the slopes of the Stern−Volmer plots, K_{sv} values ($K_{SV} = k_q\tau_0$) were calculated. Stern−Volmer plots of $I_0/I - 1$ and $\tau_0/\tau - 1$ versus [Q] for both pyrene and *tert*-butylpyrene are given in

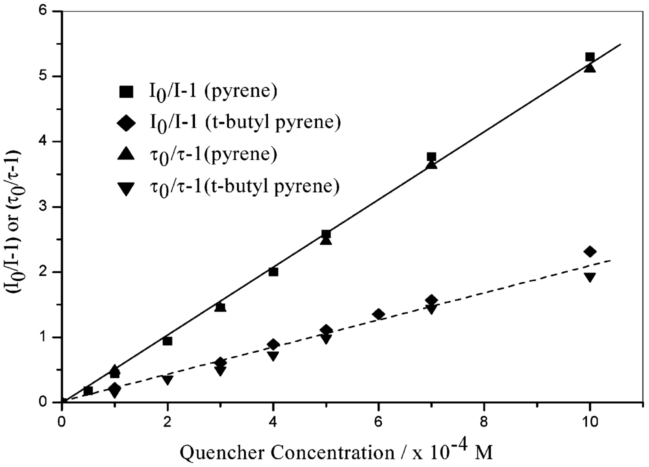


Figure 3. Stern−Volmer plots generated from both intensity and excited-state lifetime quenching of Ir(ppy)$_3$ photoluminescence measured as a function of pyrene or di-*tert*-butylpyrene concentration in CH_2Cl_2.

Figure 3 and clearly demonstrate pure dynamic quenching in both instances. The K_{sv} values for pyrene and *t*-butylpyrene are 5145 M^{-1} and 2255 M^{-1}, respectively, thereby yielding bimolecular quenching constants of k_q(pyrene) = 2.23×10^9 M^{-1} s^{-1} and k_q(*tert*-butylpyrene) = 9.79×10^8 M^{-1} s^{-1}. The quenching pathway in both cases is presumed to proceed through triplet energy transfer on the basis of the positions of the relevant energy levels. In addition, the observation of upconverted fluorescence, see below, must result from a TTA mechanism which implies efficient triplet production in the MLCT quenching step. On the basis of the Stern−Volmer data, it is clear that triplet energy transfer from Ir(ppy)$_3$ is more favorable with pyrene as quencher, and in both instances, nearly complete sensitizer quenching is expected in the millimolar concentration range. Therefore, all upconversion experiments were performed at a minimum concentration of 1 mM pyrene or di-*tert*-butylpyrene.

Selective excitation of Ir(ppy)$_3$ in deaerated CH_2Cl_2 solutions containing pyrene, using the 450 ± 2 nm output of a N_2-pumped dye laser with pulse energies varying from 8 to 70 μJ, yields a clearly observable delayed upconverted fluorescence signal at shorter wavelengths, with an onset near 360 nm. Since the upconverted fluorescence is produced by long wavelength sensitization, the signal is free from artifacts such as prompt singlet fluorescence. Figure 4A displays the upconverted fluorescence spectrum of pyrene (1×10^{-3} M) sensitized by Ir(ppy)$_3$ (1×10^{-5} M), measured 30 μs after a 450 ± 2 nm, 32 μJ laser pulse. The prompt fluorescence emitted from pyrene through direct excitation at 340 nm as measured in a steady-state fluorimeter is included for comparative purposes, Figure 4B. Both spectra contain contributions from singlet fluorescence at shorter wavelengths (360−420 nm) and excimer emission at longer wavelengths, centered near 470 nm. Although excimer production results in the degradation of energy stored in the TTA-sensitized singlet excited state, the current work illustrates a plausible method for sensitizing pyrene excimers using long wavelength photons. While this result is intriguing, we are uncertain of potential applications or the possible ramifications of harnessing such processes. The efficiency of excimer production (at 1 mM pyrene) is likely greater than 1% as the blue emission emanating from this species is readily discernible with the naked eye in a lighted room in a single 32 μJ, 450-nm laser pulse. This result implies that the upconversion quantum efficiency must be somewhat larger; however, in the absence of an absolute quantum yield determination, we emphasize that this efficiency estimate is speculative. The identical upconversion experiments performed using di-*tert*-butylpyrene and Ir(ppy)$_3$ are shown in Figure 5 and clearly demonstrate the suppression of excimer formation at long wavelengths. The fact that the upconverted fluorescence spectrum is almost the same as the prompt fluorescence spectrum in both cases demonstrates that the upconverted fluorescence signals in both cases emanate from the singlet states of pyrene (or pyrene excimer) or di-*tert*-butylpyrene which are produced via triplet−triplet annihilation. Long wavelength laser excitation of the individual chromophores failed to produce upconverted fluorescence in all instances.

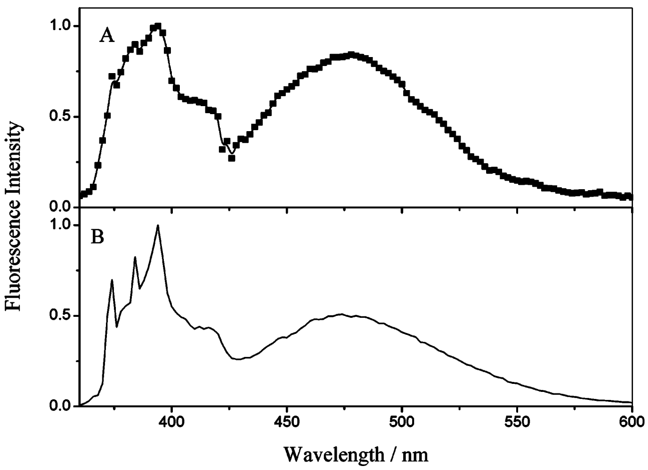


Figure 4. (A) Delayed fluorescence spectrum measured in a CH_2Cl_2 solution containing pyrene (1×10^{-3} M) and Ir(ppy)$_3$ (1×10^{-5} M) measured 30 μs after a 450 ± 2 nm, 32 μJ laser pulse. (B) Prompt steady-state fluorescence spectrum of pyrene (1×10^{-3} M) in CH_2Cl_2, excited at 340 nm.

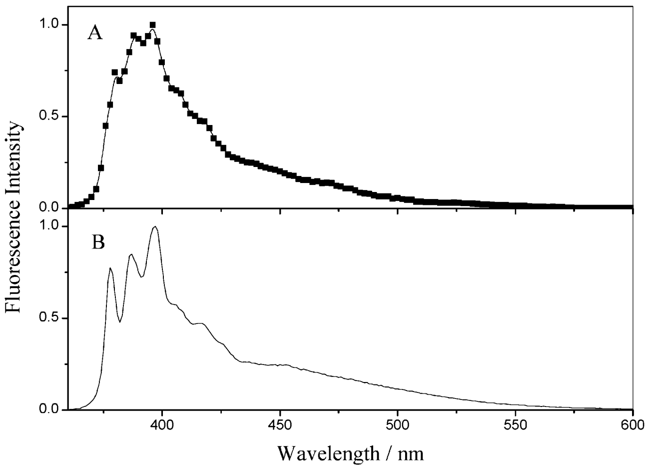


Figure 5. (A) Delayed fluorescence spectrum measured in a CH_2Cl_2 solution containing di-*tert*-butylpyrene (1×10^{-3} M) and Ir(ppy)$_3$ (1×10^{-5} M) measured 30 μs after a 450 ± 2 nm, 32μJ laser pulse. (B) Prompt steady-state fluorescence spectrum of di-*tert*-butylpyrene (1×10^{-3} M) in CH_2Cl_2, excited at 340 nm.

The dependence of the intensity of upconverted fluorescence on incident laser pulse energy was evaluated for both quenchers. Single wavelength time-resolved photoluminescence data was integrated for each sample as a function of incident laser power, these data were normalized to the highest incident power. As shown in Figure 6, the upconverted fluorescence intensity emitted from pyrene and *tert*-butylpyrene at 390 ± 8 nm increases in a nonlinear fashion as a function of increasing the laser pulse energy from 8.7 μJ/pulse to 67.9 μJ/pulse. The dashed line represents the best quadratic fit to the nonlinear

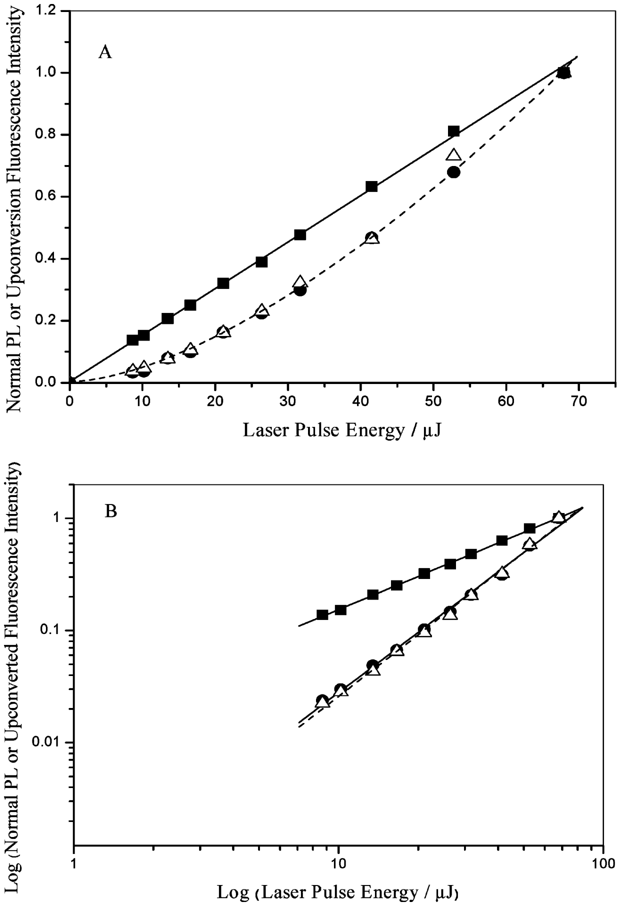


Figure 6. (A) Delayed integrated fluorescence intensities measured in mixtures of Ir(ppy)$_3$/pyrene (△) and Ir(ppy)$_3$/di-*tert*-butylpyrene (●) at 390 nm and prompt photoluminescence intensity of Ir(ppy)$_3$ at 515 nm (■) measured as a function of 450 ± 2 nm incident pulse energy in deaerated CH$_2$Cl$_2$. The data are normalized to the highest incident intensity. The solid line is the best linear fit to the Ir(ppy)$_3$ data and the dashed line is the best quadratic fit to the upconverted fluorescence data for the Ir(ppy)$_3$/pyrene system. (B) Double logarithm plot of the data in A; the slopes are 0.98 for Ir(ppy)$_3$, 1.83 for Ir(ppy)$_3$/pyrene, and 1.78 for Ir(ppy)$_3$/di-*tert*-butylpyrene.

curve generated in the case of pyrene, and the raw data used in the generation of this plot is provided as Supporting Information. The data obtained in the case of *tert*-butylpyrene shows an almost identical curvature which supports the nonlinear excitation mechanism afforded by sensitized TTA. For comparison, decay curves were measured for unquenched Ir(ppy)$_3$ photoluminescence as a function of laser power and resulted in the expected linear excitation power dependence, Figure 6. The data presented in Figure 6A were more closely evaluated by making double logarithm plots which better differentiate one- and two-photon excitation processes, Figure 6B. The slope of the solid line associated with the solid squares in Figure 6B is 0.98 indicative of the one-photon excitation processes associated with the generation of Ir(ppy)$_3$ MLCT emission[13] and also shows that our time-resolved instrumentation is linear over the photoluminescence intensity ranges studied. The solid and dashed lines associated with the open triangles and filled circles have slopes of 1.83 and 1.78, respectively. Ideally, these slopes would have values of 2.00 which would unequivocally indicate a two-photon excitation process.[1−9] In the present case, both values quantitatively match within experimental error and approach the ideal two-photon slope, therefore, we conclude that the nonlinear data adequately represents two sequential one-photon excitations. This is indicative of the quadratic dependence of the triplet−triplet annihilation process, where the upconverted fluorescence intensity measured for both pyrene quenchers is proportional to the square of the incident laser power and hence to the square of the triplet concentration.[13,14]

Conclusions

The present contribution demonstrates the observation of upconverted fluorescence from pyrene and *tert*-butylpyrene resulting from triplet−triplet annihilation sensitized to visible light using Ir(ppy)$_3$. Compared to our earlier reports,[13,14] the upconverted singlet fluorescence energy has been increased to 3.44 eV by using a combination of higher energy triplet sensitizer and aromatic hydrocarbons with higher energy singlet/triplet levels. In cases where pyrene was used as the quencher/annihilator, pyrene excimers were produced following triplet quenching and TTA, in essence degrading the energy stored in the pyrene singlet state. To circumvent energy-wasting excimer production, *tert*-butylpyrene was employed as the triplet quencher/annihilator. The steric bulk afforded by the two tert-butyl groups effectively shunted the excimer-forming pathway, permitting clean observation of upconverted singlet fluorescence. In both instances, the incident photon power dependence is consistent with two sequential one-photon excitations, supporting the sensitized TTA mechanism as responsible for the production of the upconverted fluorescence. The current work demonstrates that sensitized TTA is indeed accessible to chromophore systems beyond those previously reported, suggesting the generality of this approach. Therefore, the energy of upconverted fluorescence may still be improved by using appropriate inorganic triplet donors and other organic acceptors/annihilators. Such future molecular upconverters would undoubtedly find niche applications in photonics.

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Supporting Information Available: Time-resolved upconversion intensity decay profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Albota, M.; Beljonne, D.; Bredas, J.-L.; Ehrlich, J. E.; Fu, J.-Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653−1656.

(2) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863−1874.

(3) Chung, S.-J.; Kim, K.-S.; Lin, T.-C.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem. B* **1999**, *103*, 10741−10745.

(4) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I.-Y. S.; McCord-Maughon, D.; Qin, J.; Rockel, H.; Rumi, M.; Wu, X.-L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51−54.

(5) Zhou, W.; Kuebler, S. M.; Braun, K. L.; Yu, T.; Cammack, J. K.; Ober, C. K.; Perry, J. W.; Marder, S. R. *Science* **2002**, *296*, 1106−1109.

(6) Stellacci, F.; Bauer, C. A.; Meyer-Friedrichsen, T.; Wenseleers, W.; Alain, V.; Kuebler, S. M.; Pond, S. J. K.; Zhang, Y.; Marder, S. R.; Perry, J. W. *Adv. Mater.* **2002**, *14*, 194−198.

(7) Bartholomew, G. P.; Rumi, M.; Pond, S. J. K.; Perry, J. W.; Tretiak, S.; Bazan, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 11529−11542.

(8) Drobizhev, M.; Stepanenko, Y.; Dzenis, Y.; Karotki, A.; Rebane, A.; Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **2004**, *126*, 15352−15353.

(9) LaFratta, C. N.; Baldacchini, T.; Farrer, R. A.; Fourkas, J. T.; Teich, M. C.; Saleh, B. E. A.; Naughton, M. J. *J. Phys. Chem. B* **2004**, *108*, 11256−11258.

(10) (a) Parker, C. A.; Hatchard, C. G. *Proc. Chem. Soc., London* **1962**, 386−387. (b) Parker, C. A. *Adv. Photochem.* **1964**, *2*, 305−383.

(11) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968.

(12) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

(13) Kozlov, D. V.; Castellano, F. N. *Chem. Commun.* **2004**, 2860−2861.

(14) Islangulov, R. R.; Kozlov, D. V.; Castellano, F. N. *Chem. Commun.* **2005**, 3776−3778.

(15) Islangulov, R. R.; Castellano, F. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 5957−5959.

(16) (a) Baluschev, S.; Yu, F.; Miteva, T.; Ahl, S.; Yasuda, A.; Nelles, G.; Knoll, W.; Wegner, G. *Nano. Lett.* **2005**, *5*, 2482−2484. (b) Keivanidis, P. E.; Baluschev, S.; Miteva, T.; Nelles, G.; Scherf, U.; Yasuda, A.; Wegner, G. *Adv. Mater.* **2003**, *15*, 2095−2098. (c) Laquai, F.; Wegner, G.; Im, C.; Busing, A.; Heun, S. *J. Chem. Phys.* **2005**, *123*, 074902.

(17) (a) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750−753. (b) Nazeeruddin, Md. K.; Humphry-Baker, R.; Berner, D.; River, S.; Zuppiroli, L.; Graetzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 8790−8797. (c) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377−7387. (d) Lamansky, S.; Djurovich, P. I.; Murphy, P.; Abdel-Razzaq, F.; Lee, H. E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304−4312.

(18) Noh, Y.; Lee, C.; Kim, J.; Yase, K. *J. Chem. Phys.* **2003**, *118*, 2853−2864.

(19) Tang, K.; Liu, K.; Chen, I. *Chem. Phys. Chem.* **2004**, *386*, 437−441.

(20) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(21) (a) Ilharco, L. M.; Santos, A. M.; Silva, M. J.; Martinho, J. M. G. *Langmuir* **1995**, *11*, 2419−2422. (b) Lewis, F. D.; Zhang, Y.; Letsinger, R. L. *J. Org. Chem.* **1997**, *62*, 8565−8568. (c) Cheng, K.; Schepp, N. P.; Cozens, F. L. *J. Phys. Chem. A* **2004**, *108*, 7132−7134. (d) Thomas, A.; Polarz, S.; Antonietti, M. *J. Phys. Chem. B* **2003**, *107*, 5081−5087. (e) Martins, J.; Vaz, W. L. C.; Melo, E. *J. Phys. Chem.* **1996**, *100*, 1889−1895.

(22) Dedeian, K.; Djurovich, P. I.; Garces, F. O.; Calson, G.; Watts, R. J. *Inorg. Chem.* **1991**, *30*, 1685−1687.

(23) Buu-Hoi; Cagniant, P. *Chem. Ber.* **1944**, *77B*, 121−6.

(24) (a) Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, *103*, 10955−10960. (b) Tyson, D. S.; Luman, C. R.; Zhou, X.; Castellano, F. N. *Inorg. Chem.* **2001**, *40*, 4063−4071. (c) Tyson, D. S.; Henbest, K. B.; Bilecki, J.; Castellano, F. N. *J. Phys. Chem. A* **2001**, *105*, 8154−8161.

(25) Wang, Y.; Herron, N.; Grushin, V. V.; Lecloux, D.; Petrov, P. *Appl. Phys. Lett.* **2001**, *79*, 449−451.

(26) Karpovich, D. S.; Blanchard, G. J. *J. Phys. Chem.* **1995**, *99*, 3951−3958.

(27) Eastman, J. W. *Photochem. Photobiol.* **1967**, *6*, 55−72.

(28) (a) Suib, S. L.; Kostapapas, A. *J. Am. Chem. Soc.* **1984**, *106*, 7705−7710. (b) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039−2044.