J|A|C|S
COMMUNICATIONS

Published on Web 11/23/2002

Bis-cyclometalated Ir(III) Complexes as Efficient Singlet Oxygen Sensitizers

Ruomei Gao,[†] David G. Ho,[†] Billy Hernandez,[†] Matthias Selke,*[,†] Drew Murphy,[‡] Peter I. Djurovich,[‡] and Mark E. Thompson*[,‡]

Department of Chemistry, California State University at Los Angeles, Los Angeles, California 90032, and Department of Chemistry, University of Southern California, Los Angeles, California 90089

Received August 8, 2002

The chemistry of cyclometalated Ir(III) complexes has received a great deal of attention recently. These complexes have proven to be very efficient emissive dopants in molecular and polymeric light-emitting diodes.[1] While studying the photophysical properties of these complexes, it was noticed that the quantum efficiencies and triplet lifetimes are severely reduced by oxygen,[1a,2] only giving high values ($\phi > 0.5$ and $\tau > 2$ μs) for rigorously degassed samples. This prompted us to investigate these complexes as potential singlet oxygen sensitizers, as singlet oxygen formation is a possible quenching process. We now report that a variety of bis-cyclometalated Ir(III) complexes are indeed useful photosensitizers for the production of singlet oxygen, with generally high quantum efficiencies and small concomitant physical quenching of singlet oxygen.

The Ir(III) complexes employed in this study are depicted in Figure 1.[3] The lowest energy (emissive) excited state of these complexes is a mixture of MLCT and $^3(\pi-\pi^*)$ states,[1a] composed principally of C^N ligand orbitals, with the β-diketonate ligand (Figure 1, L^X = BSN, BSN*, BT, and PQ) acting as an ancillary ligand. Stern−Volmer analysis shows that phosphorescence from these complexes is efficiently quenched by triplet oxygen, at near diffusion controlled rates (Table 1).

The efficient oxygen quenching does involve the formation of singlet oxygen, as all of the Ir complexes studied here proved to be excellent singlet oxygen sensitizers. The quantum yields for singlet oxygen production (Φ_Δ) are given in Table 1. The quantum yields were obtained by measuring the intensity of the $^1O_2$ luminescence signal ($\lambda_{max} = 1268$ nm). Measurements were taken with 355 and 532 nm excitation, in air-saturated solutions. Triplet−triplet annihilation was negligible at these concentrations, as evidenced by the fact that the $^1O_2$ intensity does not decrease at higher concentrations (Figure 2), as it would if T−T annihilation were depleting the excited sensitizer. The singlet oxygen quantum yields are very large and near unity for all of the β-diketonate complexes examined here. The Φ_Δ values are high for both ligand-based excitation (355 nm) and direct excitation of the lowest energy excited state (MLCT + ^{3}LC) with 532 nm light.

Ir complexes are known to form singlet oxygen upon optical excitation (e.g., $[Ir(bpy)_3]^{3+}$ and $[Ir(phen)_3]^{3+}$).[4] However, many Ir complexes also quench singlet oxygen efficiently.[5] Large $^1O_2$ quenching rates would severely limit potential applications of the bis-cyclometalated Ir complexes as photosensitizers. We therefore determined singlet oxygen quenching rates for all of the Ir complexes reported here. These quenching rate constants [$k_q(^1O_2)$] are given in Table 1. The quenching rates for all of the complexes

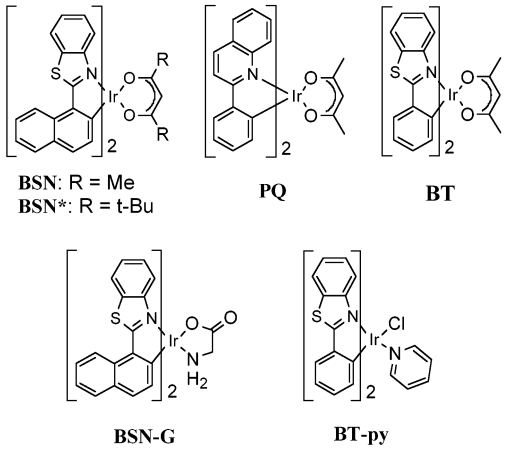


Figure 1. Structures of the singlet oxygen sensitizers used in this study.

Table 1. Quantum Yields for Singlet Oxygen Generation (Φ_Δ) with 355 or 532 nm Excitation (λ), Rate Constants for Oxygen Quenching of the Phosphorescence, Determined by Stern−Volmer Analysis ($k_{q,SV}$), and Rate Constants for Singlet Oxygen Quenching by the Ir Complex Sensitizer [$k_q(^1O_2)$]

sensitizer[a]	λ (nm)	Φ_Δ[b]	$k_{q,SV}$ (10^9 M^{-1} s^{-1})	$k_q(^1O_2)$ (10^6 M^{-1} s^{-1})
BSN	355	0.59 ± 0.07		6.3 ± 0.2
	532	0.89 ± 0.02		
BSN*	355	0.60 ± 0.06	2.9 ± 0.1	4.0 ± 0.3
	532	0.77 ± 0.08		
PQ	355	0.62 ± 0.05	7.2 ± 0.3	1.0 ± 0.2
	532	0.89 ± 0.07		
BT	355	0.86 ± 0.07	5.9 ± 0.6	0.5 ± 0.2
	532	1.00 ± 0.07		
BSN-G	355	0.54 ± 0.02		2.1 ± 0.5
	532	0.81 ± 0.06		
BT-py	355	0.95 ± 0.09		none
	532	1.00 ± 0.09		detected

[a] Measurements were made in C_6H_6 solvent. [b] The references for quantum yield measurements were C_{60} (0.76), TPP (0.62), and perinaphthenone (0.95) at 355 nm and TPP (0.62) at 532 nm.

with β-diketonate ancillary ligand were found to be small, ranging from $(10 \pm 2) \times 10^5$ M^{-1} s^{-1} for PQ to $(6 \pm 0.2) \times 10^6$ M^{-1} s^{-1} for BSN. These singlet oxygen quenching rates are roughly 3 orders of magnitude slower than the phosphorescence quenching rates (k_{qSV}), consistent with the high Φ_Δ values observed here. For the BT complex, the singlet oxygen quenching rate is in fact smaller than those of many standard singlet oxygen sensitizers such as tetraphenylporphyrin (TPP) [$k_q = (6 \pm 2) \times 10^7$ M^{-1} s^{-1}],[6] while the quantum yield is near unity. Even though the four cyclometalling ligands used here give rise to very different absorption and emission energies,[1a,3] their efficiencies for singlet oxygen production are very similar. On the basis of spectroscopic measurements for these four

* To whom correspondence should be addressed. E-mail: mselke@calstatela.edu.
[†] California State University at Los Angeles.
[‡] University of Southern California.

10.1021/ja0280729 CCC: $22.00

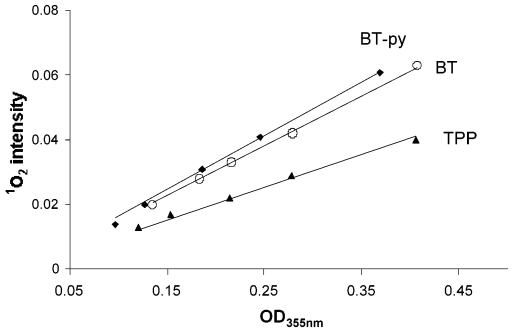
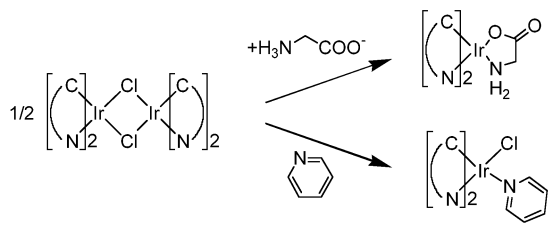


Figure 2. Relative intensity of singlet oxygen production vs absorbance for BT, BT-py, and TPP at 355 nm ($OD_{355\ nm}$).

complexes,[1a] the orbital makeups for the triplet excited states are similar and largely ligand based (i.e., $\pi-\pi^*$). Hence, it is not too surprising that they have similar efficiencies for $^1O_2$ generation. The slight decrease of Φ_Δ of BSN at 532 nm relative to BSN* at 532 nm appears to be out of the error range and may be due to a steric blocking effect.

All of the sensitizers with β-diketonate ancillary ligands are resistant toward irradiation under aerobic conditions, as we have detected no significant decomposition for irradiation times of up to 60 min. Thus, we expect that singlet oxygen sensitization may only marginally affect the lifetimes of light-emitting diodes doped with these Ir-based emitters.[7]

Singlet oxygen is capable of damaging nucleic acids, proteins, and lipids in the cellular environment. The reactions of singlet oxygen with nucleotide bases and amino acids have been the subject of intensive research for several decades.[8] However, there have been few studies on the variation of Φ_Δ upon attachment of the sensitizer to an amino acid residue. While the β-diketonate ligands used in BSN, PQ, and BT are useful ancillary ligands, they are not good models for biologically relevant ligands. To investigate the potential of our cyclometalated Ir complexes as singlet oxygen sensitizers when coordinated to biomolecules, we prepared Ir complexes with glycine and pyridine/chloride (Figure 1, L^X = BSN-G and BT-py, respectively). The attachment of the Ir complex to a given Lewis basic group is a straightforward process.[9] The Cl bridged dimer is readily cleaved by Lewis basic groups, such as pyridine or glycine, to give the desired Ir complex; see equation below. The glycine derivatives form a chelated structure (BSN-G), while the pyridyl derivatives retain a terminal Cl ligand (BT-py). The pyridyl group is a good model for the imidazole side group of histidine, while the coordinated glycine models both amine side groups, such as those of lysine, and carboxylic acid side groups, such as those of aspartic and other carboxyl containing amino acids.



The singlet oxygen quantum yield for BSN-G is similar to that of the related β-diketonate complexes, consistent with the "(C^N)$_2$Ir" fragment being responsible for the observed photophysics. The pyridyl derivative (BT-py) also shows a high quantum yield for singlet oxygen production and no measurable singlet oxygen quenching. Neither the presence of a terminal chloride nor the nonchelating nature of the single Lewis basic ligand prevents the efficient formation of singlet oxygen by these complexes.

The high quantum yields for the glycine and pyridyl complexes and the remarkable ease by which amino acids can be attached to the sensitizers demonstrate that these sensitizers could indeed be used to study oxidative damage to the peptide chain via photogenerated singlet oxygen. The fact that a wide range of different Ir dimer complexes are accessible[1a] and can be easily attached to side groups of histidine, other amino acids, and other biomolecules[2a] makes them particularly good candidates for use as selective photooxidizing agents for biological materials. We are currently investigating amino acid side chain functionalities and other biologically relevant groups as ligands for cyclometalated Ir(III) complexes as well as their ability to sensitize singlet oxygen.

Acknowledgment. The authors wish to thank Ms. Joelle Underwood and Professor Curt Wittig for help with lifetime measurements. We gratefully acknowledge support from the NIH-NIGMS MBRS program (Award number GM 08101) and DARPA (Grant number MDA972-01-1-0032).

Supporting Information Available: Preparative and characterization data for the sensitizers, the details of the Stern−Volmer analysis for quenching of phosphoresecence by triplet dioxygen, as well as the details of singlet oxygen quantum yield measurements, and singlet oxygen luminescence quenching plots for all sensitizers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Lamansky, S.; Djurovich, P.; Murphy, D.; 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. (b) Lamansky, S.; Kwong, R. C.; Nugent, M.; Djurovich, P. I.; Thompson, M. E. *Org. Electrochem.* **2001**, *2*, 53−62. (c) Ikai, M.; Tokito, S.; Sakamoto, Y.; Suzuki, T.; Taga, Y. *Appl. Phys. Lett.* **2001**, *79*, 156−158. (d) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *J. Appl. Phys.* **2001**, *90*, 4058. Yang, M.-J.; Tsutsui, T. *Jpn. J. Appl. Phys.* **2000**, *39*, L828−L829.

(2) (a) Lo, K. K.-W.; Ng, D. C.-M.; Chung, C.-K. *Organometallics* **2001**, *20*, 4999−5001. (b) Di Marco, G.; Lanza, M.; Mamo, A.; Stefio, I.; Di Pietro, C.; Romeo, G.; Campagna, S. *Anal. Chem.* **1998**, *70*, 5019−5023. (c) Amao, Y.; Ishikawa, Y.; Okura, I. *Anal. Chim. Acta* **2001**, *445*, 177−182.

(3) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704−1711. The synthetic procedures and characterization data are given in the Supporting Information.

(4) Demas, J. N.; Harris, E. W.; McBride, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 3547−3551. Demas, J. N.; Harris, E. W.; Flynn, C. M.; Diemente, D. *J. Am. Chem. Soc.* **1975**, *97*, 3838−3839.

(5) Selke, M.; Foote, C. S.; Karney, W. L. *Inorg. Chem.* **1995**, *34*, 5715−5720.

(6) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423−3430.

(7) Moreover, these devices must be packaged under anaerobic conditions to maintain long lifetime, which will prevent oxygen from reaching the sensitizer.

(8) (a) Cadet, J.; Vigny, P. In *The Photochemistry of Nucleic Acids*; Morrison, H., Ed.; John Wiley and Sons: New York, 1990; pp 1−272. (b) Foote, C. S.; Clennan, E. L. In *Active Oxygen in Chemistry*; Foote, C. S., Valentine, J. S., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic and Professional (Chapman & Hall): New York, 1995; Chapter 4.

(9) Urban, R.; Kramer, R.; Mihan, S.; Polborn, K.; Wagner, B.; Beck, W. *J. Organomet. Chem.* **1998**, *517*, 191−200.

JA0280729