Generation of Singlet Oxygen via Excited State Reactions

Matthew White[1], Qingxin Chen[2] , Russell Schmehl[2]
[1]Uinversity of the Incarnate Word, [2]Tulane University

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Introduction

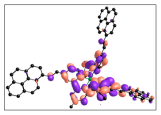
Photodynamic Therapy (PDT) can be used to treat a variety of different skin cancers. To do this, a photosensitizer is applied to the area of skin affected and light at a specific wavelength allows a series of reactions to occur. The photosensitizer will go through a variety of different excited states and produce singlet oxygen inside of the cancerous skin cells. However, it is only produced near the area where the photosensitizer was applied. This ensures that only cancerous cells that are targeted and healthy cells are unaffected by the treatment. This method also prevents cancer cells from becoming chemically resistant to treatment.

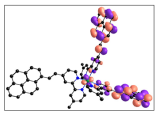
Chromophores for PDT

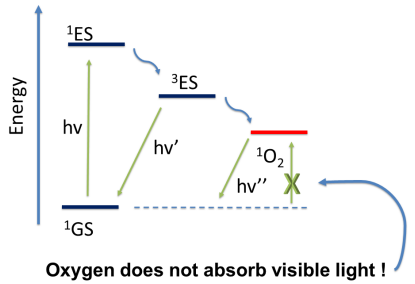
For the photosensitizer in PDT to produce singlet oxygen, it needs to be able to absorb wavelengths of light that penetrate the skin. At 600 nm, the light will penetrate the skin about 0.5 cm, and 700 nm to 800 nm will penetrate the skin to about 1 cm. Because the goal is only to kill skin cancer cells at the surface, it is beneficial to limit the amount of light that penetrates the skin. The optimal wavelength is around 600 nm. Light that comes from the source is intense and can also damage healthy cells if it not controlled. The objective in this work is to develop a new chromophore for PDT that is a better sensitizer or reactive singlet oxygen.

Energy Levels

The active photosensitizer targeted is $[Ru(pyr\text{-}v\text{-}bpy)_3]^{2+}$.
When this chemical is initially excited from the light, electrons will jump to the singlet state (^{1}ES) with higher energy. Electrons will then jump down to a lower energy level and form a triplet state (^{3}ES).
This excited state can then transfer energy to oxygen within cells, creating the reactive species necessary to kill the cells ($^1O_2$) .

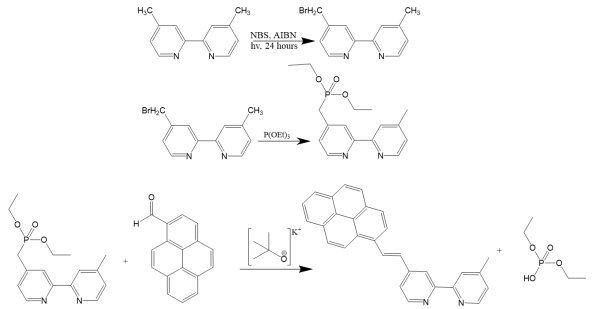

LUMO


HOMO

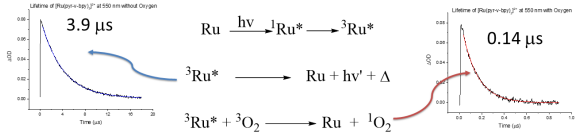


Oxygen does not absorb visible light !

Synthesis of Ligand

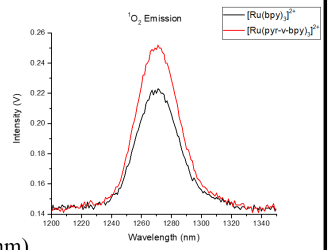


Excited State Quenching of Ru complex with O_2



$^1O_2$ emission of $[Ru(bpy)_3]^{2+}$ vs $[Ru(pyr\text{-}v\text{-}bpy)_3]^{2+}$

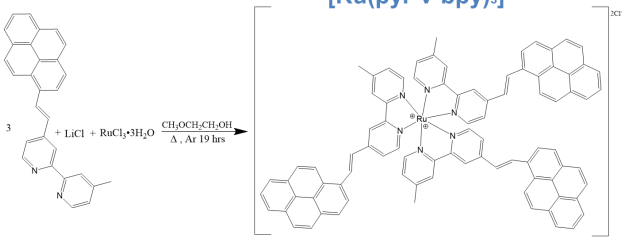
Both Ru complexes were able to produce singlet oxygen and the distinct emission at 1270 nm. However, there was a higher yield of $^1O_2$ from $[Ru(pyr\text{-}v\text{-}bpy)_3]^{2+}$ than $[Ru(bpy)_3]^{2+}$. This makes it a better photo-sensitizer to produce singlet Oxygen.



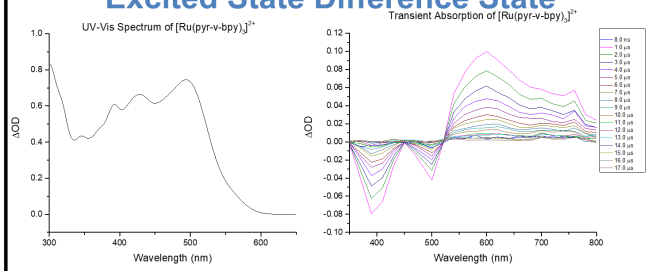
$^1O_2 \longrightarrow {}^3O_2 + hv''$ (1270 nm)

Ruthenium Complex Synthesis

$[Ru(pyr\text{-}v\text{-}bpy)_3]^{2+}$



Excited State Difference State



Physical Property at 550 nm	$[Ru(pyr\text{-}v\text{-}bpy)_3]^{2+}$
τ with O_2, µs	0.136
$K_r+K_n+K_q$ $[O_2]$with O_2, s^{-1}	7.35E+06
τ without O_2, µs	3.89
K_r+K_n without O_2, s^{-1}	2.57E+05
K_q (2.4mM O_2), $M^{-1}s^{-1}$	2.96E+09

Conclusion and Future Works

Experimentation on $[Ru(pyr\text{-}v\text{-}bpy)_3]^{2+}$ was successful and yielded more singlet oxygen than $[Ru(bpy)_3]^{2+}$. Future research will analyze the interaction between singlet oxygen produced and the Ru complex. Does the singlet oxygen attack and degrade the complex?

References

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