Singlet O$_2$ Quantum Yield

This method is a modified version of that used in the following references. [1] [2] [3]

You will need to prepare 3 stock solutions, one of DPBF, one of [Ru(bpy)$_3$]Cl$_2$ and one of sample to be tested. All solutions must be made in the dark, especially the DPBF which slowly decays over time when exposed to light. Best to store the stock solutions in a draw until you are ready to prepare sample solutions.

DPBF Stock

   1.1 mg of DPBF in 4.000 mL of MeOH will provide a stock solution of 1.0 mM

[Ru(bpy)$_3$]Cl$_2$ and Sample Stock

   The absorbance at 460 nm for both [Ru(bpy)$_3$]Cl$_2$ and the sample will need to be the same for both test solutions. 3.000 mL will be the final volume, concentrations of both should be adjusted to give a final absorbance of 0.01 for the test solutions. The absorbance may be adjusted up to 0.1 if needed, but lower concentration is ideal as you do not want the absorbance of the solutions at 405 nm to effect the emission of the DPBF. [Ru(bpy)$_3$]Cl$_2$ has a molar absorptivity of 13671 M$^-$cm$^-$ at 460 nm.

1. Turn on instrument and start the software as normal
2. From the Experiment Menu, select Kinetic Experiment
3. Load the Singlet O2 Quantum Yield.XML file
4. Click RTC (Real Time Control) button found at the bottom of the window
5. In the new window that opens, the following values should be displayed
   a. Excitation Slit: 3 nm
   b. Emission Slit: 3 nm
   c. Excitation Position: 460 nm
   d. Emission Position: 479 nm
   e. Integration Time: 0.1 s
6. Slit widths, Emission Position, and Integration Time should not be changed at any point. Excitation Position will need to be adjusted from the 460 nm used for photolysis, to 405 nm to collect emission data. This may easily be accomplished by entering 55 nm to the right of the + and – buttons under Excitation Position.
7. Prepare first sample solutions for DPBF, [Ru(bpy)$_3$]Cl$_2$, and each of your samples to run. Each must be run at least 3 times with a sample freshly prepared in the dark. The following shows an example setup:
   a. The DPBF stock solution has a concentration of 1.0 mM. The sample solution should have around 1.0 μM of DPBF, therefore, 3.0 μL will be required for a 3.000 mL sample.
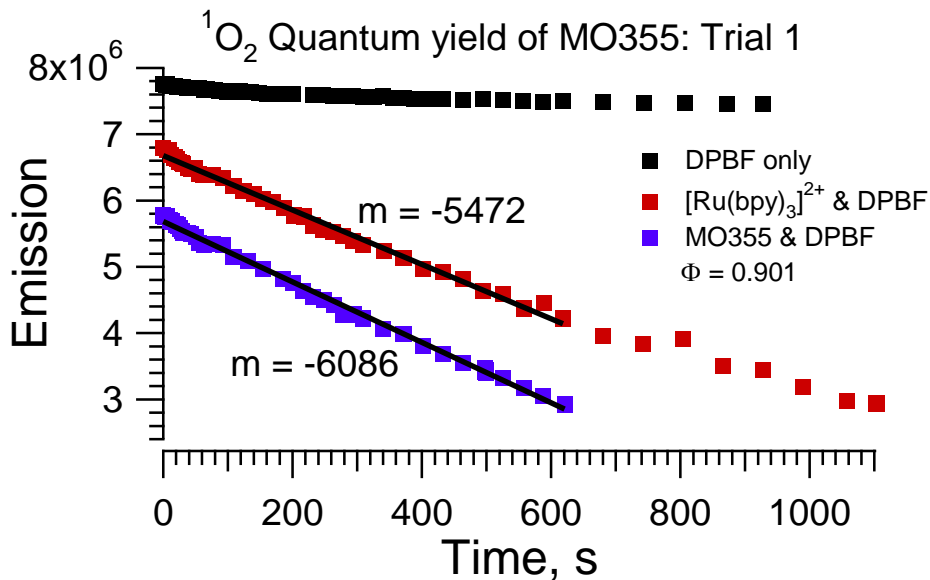
b. $[Ru(bpy)_3]Cl_2$ stock solution is known to have a concentration of 225 μM based on its absorbance at 460 nm. For a 3.000 mL sample solution to have an absorbance of 0.01 at 460 nm a concentration of 7.3 μM $[Ru(bpy)_3]Cl_2$ is needed. Therefore, 97 μL of stock solution will be needed for the $[Ru(bpy)_3]Cl_2$ sample solution.

c. The sample to be tested stock solution was adjusted to have an absorbance of 1.00 at 460 nm. Therefore, 300 μL of stock solution will be needed for a 3.000 mL sample solution.

	DPBF	$[Ru(bpy)_3]Cl_2$ + DPBF	Sample + DPBF
MeOH	2997 μL	2900 μL	2697 μL
DPBF	3.00 μL	3.00 μL	3.00 μL
$[Ru(bpy)_3]Cl_2$	-	97.0 μL	-
Sample	-	-	300 μL

8. Use 435 nm long pass filter in the instrument, and place sample in sample holder. Only data points collected with 405 nm λ_{ex} will be used.

9. Make sure Continuous Measurements is unchecked. Click the Start button. The instrument will take a single data point. This will be your initial emission.

10. Check the box next to Continuous Measurements and click Start to begin irradiation time. The graph in the RTC window has datapoints as the x-axis, so you will either have to time with a stop watch, or take into consideration that 200 data points is approximately 30 s with a 0.1 s integration time. The latter is a bit easier, and data points can be converted to time in seconds by dividing by 6.47 dp/s. For example, 100 data points/6.47 data points/s = 15.5 s. If you change the integration time, you will have to recalibrate the data points / second. In the graph window, you will see the instrument recording emission, but it will be much lower intensity compared to the initial point.

11. After 15 s, click the stop button, uncheck Continuous Measurements, click Start to take a single point, check Continuous Measurements, click Start to begin irradiation time.

12. Continue in this manner, irradiate for a certain time, stop, take single data point, continue irradiation, till the slope becomes non-linear. It will be difficult to judge as the graph window will shift every 200 data points. It usually will take between 15-20 minutes for $[Ru(bpy)_3]Cl_2$, and your sample time will vary depending on if it is less efficient then $[Ru(bpy)_3]Cl_2$ (>15 min) or more efficient (<15 min).

13. Once you have reached your stopping point, you will need to manually save the scan. Click the save button at the bottom of the RTC window, near the Start/Stop button. Save the file with an appropriate name as a *.DAT file.

14. Repeat steps 9-13 three times for each sample solution.

15. The *.DAT files can then be opened in Notepad, and copy and pasted into Excel. Convert data points to time by dividing each by 6.47. Inconsequential data

(points corresponding to irradiation times) may be deleted. To accomplish this, it is easier to sort the intensity columns from largest to smallest (make sure to choose expand the selection when prompted to keep time and intensity points linked). There will be a very large difference in the size of the intensity numbers for the irradiation times versus the emission times. Delete all the smaller numbers (irradiation times) and resort the data by the time (or data point) column from smallest to largest (again expand selection when prompted).

16. The data my now be plotted with all three sample solution on the same graph, intensity on the y-axis and time on the x-axis.

$^1O_2$ Quantum yield of MO355: Trial 1

Legend:
- DPBF only
- $[Ru(bpy)_3]^{2+}$ & DPBF
- MO355 & DPBF
- $\Phi = 0.901$

m = -5472
m = -6086

17. DPBF should be relatively flat, with a slope equal (or near) zero.
18. $[Ru(bpy)_3]Cl_2$ is known to have a $^1O_2$ quantum yield of 0.81. [3]
19. $\frac{m}{m_s} = \frac{\phi_\Delta}{\phi_\Delta^s}$ Slope of sample divided by slope of standard equals $^1O_2$ quantum yield of sample divided by $^1O_2$ quantum yield of standard

$$\frac{-6086}{-5472} = \frac{\phi_\Delta}{0.81}$$

$$\phi_\Delta = \frac{-6086}{-5472} * 0.81 = 0.9009$$

20. $^1O_2$ quantum yield of the sample in this example is 0.90

Works Cited

(1) Young, R. H.; Wehrly, K.; Martin, R. L.; *J. Am. Chem. Soc.* **1971**, 93:22, 5774.

(2) Bhattacharyya, K.; Das, P. K.; *Chem. Phys. Letters* **1985**, 116, 326.

(3) Ding, H-Y.; Wang, X-S.; Song, L-Q.; Chen, J-R.; Yu, J-H.; Li, C.; Zhang, B-W.; *J. Photochem. Photobio. A* **2006**, 177, 286-294.