University of Massachusetts Boston
Department of Chemistry
Chemistry Doctoral Program
Green Chemistry Track

July 18, 2011

Written Qualifying Exam
Inorganic Chemistry

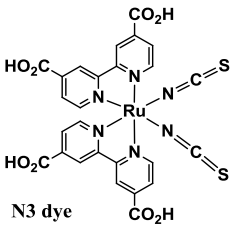
Questions are based on the following article:
Kiyoshi C. D. Robson, Bryan D. Koivisto, Aswani Yella, Barbora Sporinova, Mohammad K. Nazeeruddin, Thomas Baumgartner, Michael Graetzel, and Curtis P. Berlinguette. "Design and Development of Functionalized Cyclometalated Ruthenium Chromophores for Light-Harvesting Applications". *Inorganic Chemistry* **2011**, 50, 5494–5508.

QUESTIONS

1. Describe using a schematic diagram the components and mode of operation of a dye-sensitized solar cell (DSSC). Is the dye essential to observe photocurrent?
   (2 points)

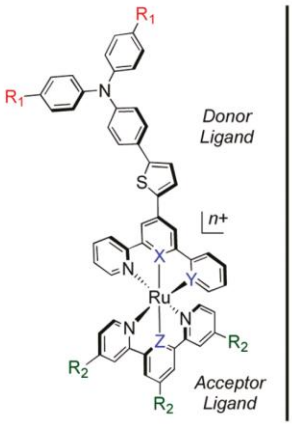
2. What does the term *orthometallated* refer to? What effect does orthometallation have on the physical properties of these dyes in comparison to the standard polypyridyl framework.
   (2 points)

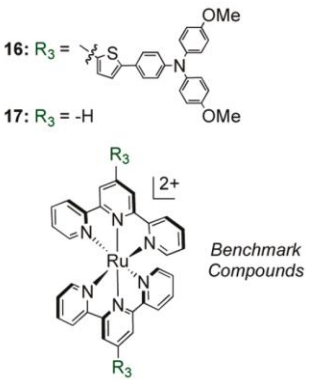
3. Robson et al. describe an elaborate series of multi-functional orthometallated dye systems for application in DSSCs. The highest reported solar-to-electric power conversion efficiency reported here is for the benchmark N3 dye at 9.3% (see below). Discuss the design criteria and strategy adapted by Robson et al. towards their novel sensitizers. The triarylamine functionality is clearly not present in the N3 structure. What role does the triarylamine moiety play in the dyes designed by Robson et al.? Does it serve its purpose and how do the authors justify its inclusion?
   (3 points)



N3 dye

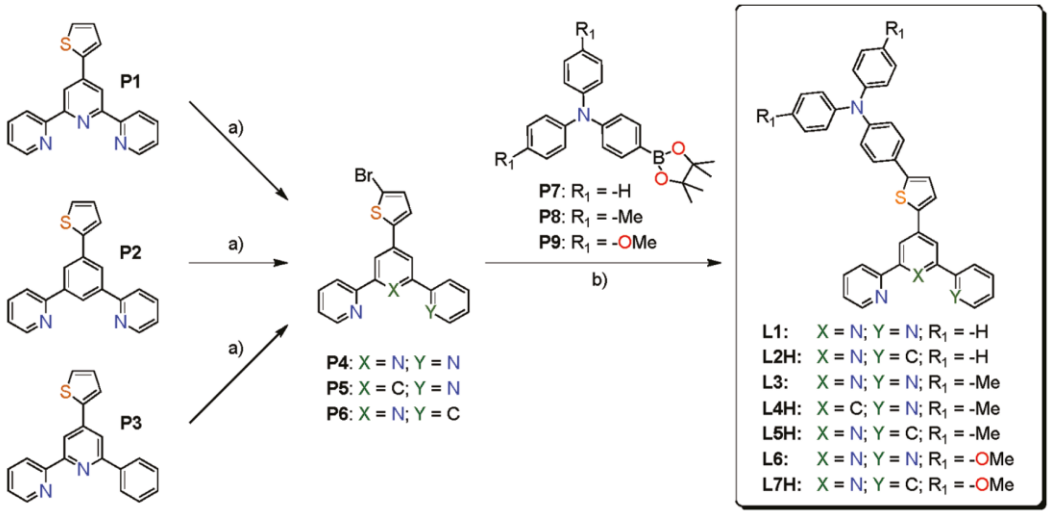
		Donor Ligand				Acceptor Ligand		
	n		-R_1	X	Y		Z	-R_2
1	2	**L1**	-H	N	N	**L8**	N	-H
2	1	**L1**	-H	N	N	**L9**	C	-H
3	1	**L2**	-H	N	C	**L10**	N	-CO_2Me
4	1	**L2**	-H	N	C	**L11**	N	-CO_2H
5	2	**L3**	-Me	N	N	**L8**	N	-H
6	1	**L3**	-Me	N	N	**L9**	C	-H
7	1	**L4**	-Me	C	N	**L8**	N	-H
8	1	**L4**	-Me	C	N	**L10**	N	-CO_2Me
9	1	**L4**	-Me	C	N	**L11**	N	-CO_2H
10	1	**L5**	-Me	N	C	**L10**	N	-CO_2Me
11	1	**L5**	-Me	N	C	**L11**	N	-CO_2H
12	2	**L6**	-OMe	N	N	**L8**	N	-H
13	1	**L6**	-OMe	N	N	**L9**	C	-H
14	1	**L7**	-OMe	N	C	**L10**	N	-CO_2Me
15	1	**L7**	-OMe	N	C	**L11**	N	-CO_2H





4. Synthesis of the precursor ligands is conducted via a Suzuki reaction. Draw a catalytic cycle for this reaction based upon one of the examples from the scheme below.
(3 points)

Scheme 1. Synthesis of Precursors P1–P9 and Ligands L1–L7[a]



[a] Reaction conditions: (a) 1 equiv of NBS, THF/AcOH (2:1), RT, 8 h; (b) $Pd(PPh_3)_4$, K_2CO_3, THF:H_2O (9:1), 65 °C, 14 h.

5. ***(Green Chemistry Question)*** The maximum power conversion efficiency for a dye-sensitized solar cell measured under standard conditions has been reported at 10.5% by the National Renewable Energy Laboratory (NREL). How does this compare to other solar cell technologies on the market. Discuss the potential of solar technologies in a future global energy economy.
(2 points)