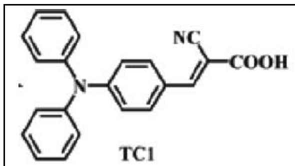
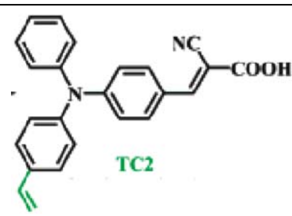
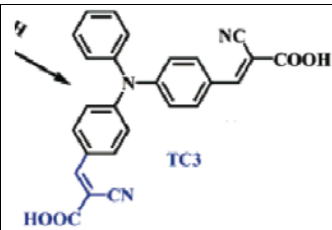
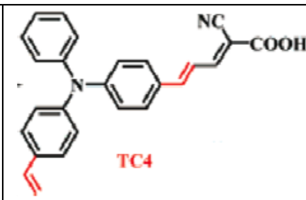
UMass Boston Green Chemistry PhD Written Qualifying Exam 6/17/08
Questions on Xu et al. paper
"New triphenylamine-based dyes for dye-sensitized solar cells"

1) Explain how dye-sensitized solar cells (DSC's) work.
   a) Draw a diagram to show the essential components of a DSC and the direction of electron flow. Label your diagram and refer to it in your answers to parts (b) and (c) below.
   b) Describe the five major molecular-level processes that occur in a DSC and, using your diagram, indicate in what regions of the DSC they occur.
   c) Which molecular level process or processes does the research presented in this paper target for improving? How will it do so? In other words, if the research in this paper is projected toward a successful conclusion, in what way(s) could DSC's become more efficient?

2) Below are the four molecules, TC1 through TC4, that were experimented with in this paper. On the last page of this exam, Figure 5 from the paper is repeated. Provide an explanation, based on the molecular structures, for the relative differences in the HOMO-LUMO gaps of the four molecules.

			
TC1	**TC2**	**TC3**	**TC4**

3) The absorption spectra of these molecules (in methanol solution) were presented in Figure 3 in the paper, which is repeated on the next page of this exam. The absorption spectra had two distinct absorption bands.
   a) The shorter wavelength absorption band was attributed to a π-π^* transition. Why does the absorption peak for this transition have a much lower intensity than the peak for the longer wavelength band?
   b) The longer wavelength absorption band was attributed to an intramolecular charge transfer mechanism. Identify the relevant features in the structures of these molecules that make this mechanism a feasible cause of an absorption band.
   c) Why is the absorption spectrum of TC4 red-shifted compared to the absorption spectra of the other three molecules?

4) The graph labeled Actinic Flux shows the solar flux at the surface of the Earth (troposphere). In the context of the Actinic Flux graph, explain why TC4 is a better dye for use in DSC's than the other three dyes tested.

5) The main conclusion of this paper is that introducing particular moieties in dyes can improve the energy conversion efficiency of DSC's.
   a) Propose a dye in the same family of dyes as those tested and draw its molecular structure. Your proposed dye should be a molecule these researchers did not study that you would hypothesize to have even better incident photon-to-current conversion efficiency than TC4.
   b) Detach the last page of this test. Use the space to the right in Figure 5 (from the paper) which is repeated on that page, and sketch what you think would be a reasonable guess for the band structure of your proposed molecule.

c) Explain why your proposed molecule would have the particular differences in HOMO and LUMO that you predict it would when compared to TC1 through TC4.

6) (Green chemistry) This question asks for estimations. Exact numbers are not important, but orders of magnitude are.

a) Why are scientists pursuing research on DSC's? Name at least one major advantage DSC's have over silicon-based solar cells?
b) The supply of energy from the Sun to the Earth is 3×10^{24} joules a year. The worldwide energy consumption rate in 2004 was 5×10^{20} joules. Estimate the fraction of Earth's surface that would need to be covered by DSC's to satisfy the world's current energy needs.
c) Identify a place in the experiments done in this paper that could be targeted for "greening." Explain why what you have chosen could be "greened" and explain how you might make it greener.

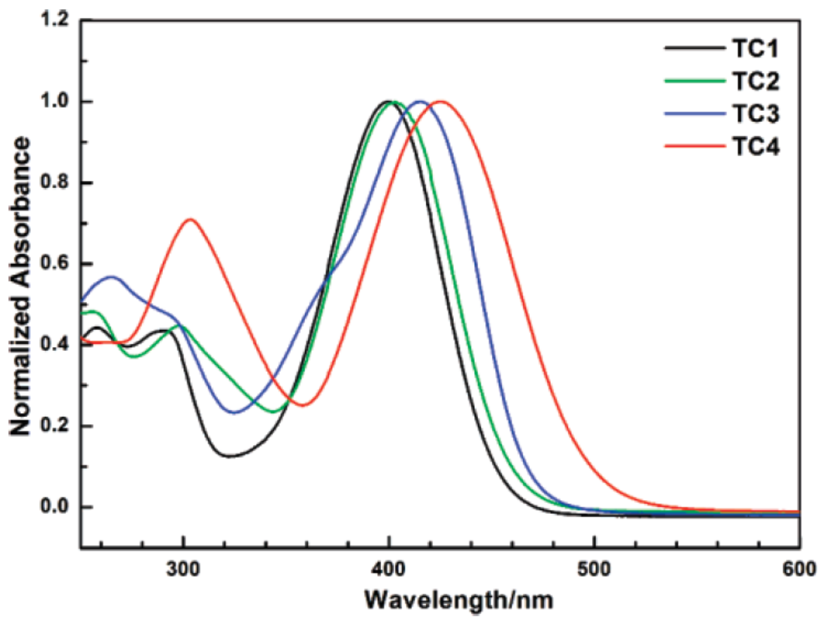


Figure 3. Normalized absorption spectra of the TC1, TC2, TC3, and TC4 measured in methanol solution.

TABLE 1: The Fluorescence Emission Properties of TC1−TC4

dye	$\lambda_{max}{}^{a}$/nm	$\epsilon_{max}{}^{a}$/M^{-1} cm^{-1}	$\lambda_{em}{}^{b}$/nm
TC1	400	15 800	554
TC2	403	29 300	542
TC3	416	18 600	548
TC4	425	26 900	585

[a, b] Absorption and emission spectra were measured in methanol solution. The emission spectra were obtained with the concentration of 5×10^{-5} M at 293 K. ϵ_{max} is the extinction coefficient at λ_{max} of absorption.

Actinic Flux

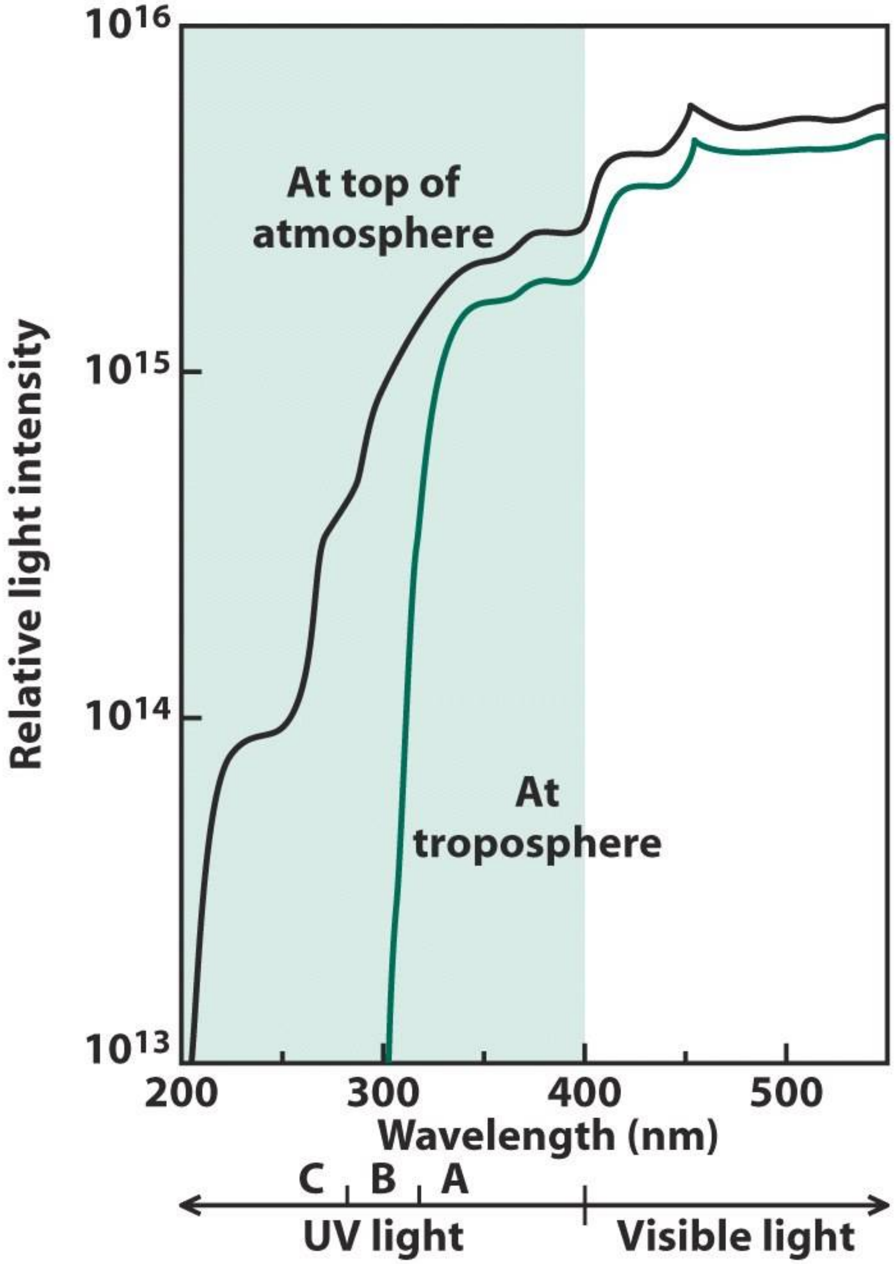


Figure 1-9
Environmental Chemistry, Third Edition

Name of Student ___________________________

This page is for use with P-Chem WQE Question 5. Please remove this paper from the test and sketch the band structure for your proposed molecule in the box. Then insert this paper in your blue book.

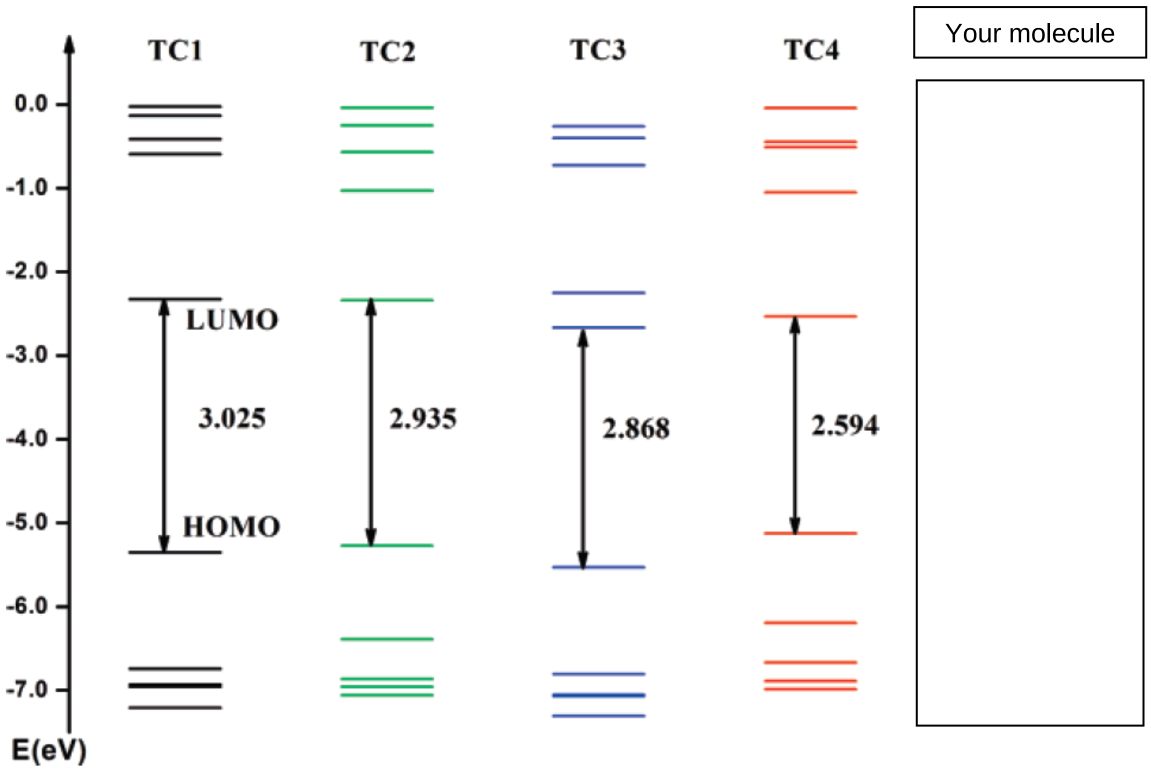


Figure 5. Schematic representation of the frontier molecular orbitals of TC1, TC2, TC3, and TC4 in methanol.