

Written Qualifying Examination - Inorganic Chemistry II

June 16, 2009

Questions related to J. Rochford, D. Chu, A. Hagfeldt, and E. Galoppini, *J. Am. Chem. Soc.*, **2007**, *129*, 4655.

The title of this paper is "Tetrachelate Porphyrin Chromophores for Metal Oxide Semiconductor Sensitization: Effect of the Spacer Length and Anchoring Group Position". Figure 1 from the paper is shown below to help you recall the compounds studied and the abbreviated naming used for them.

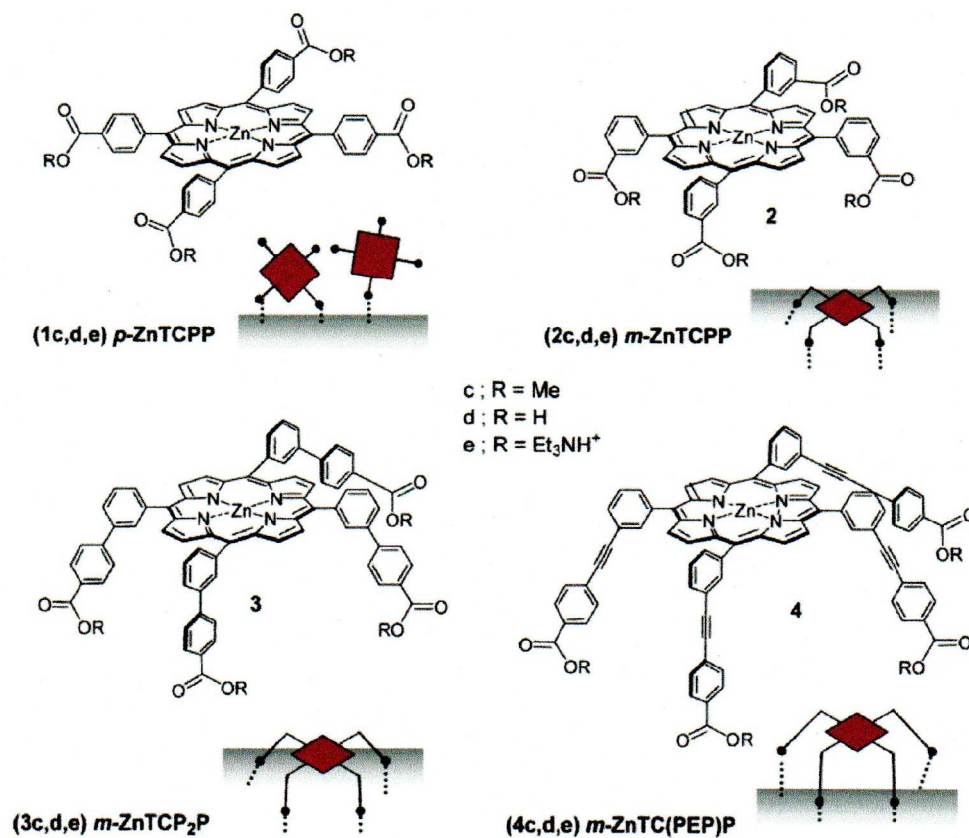


Figure 1. Structures of the porphyrins employed in this study. Also shown are the anticipated binding geometries of the COOH and COOEt₃NH derivatives on metal oxide surfaces. This diagram shows ideal behavior of the sensitizers on the metal oxide surface. However, we must assume that other binding modes are also likely. Due to the steric constraints of these systems it should take at least two of the four carboxy groups bound to the surface to fix the porphyrin chromophores in the rigid planar fashion depicted.

Questions Related to the Assigned Paper (10.0 points)

1. (2.0 points) Give a summary of the problems being addressed in this paper and the means the authors used to obtain answers to those questions.
2. (4.0 points) At various points, this paper makes use of terminology peculiar to the compounds or techniques employed. Explain the following terms, which are presented here in the contexts in which they were used in this paper.

(i) The authors state: "The carboxylic acid functionality is the most commonly used anchoring group for standard Grätzel-type DSSCs, and numerous DSSC devices employing carboxyporphyrins have been reported over the years." What are *Grätzel-type DSSCs*?

(ii) The authors state: "No atropisomers were observed for any porphyrins synthesized in this study." What are *atropisomers*? Why might the presence of atropisomers be a problem for the purposes of this study?

(iii) In describing the UV-vis absorption spectra of the compounds, the authors make reference to the Soret band. What is the *Soret band*, where in the UV-vis spectrum does it occur, and what is its state or orbital transition origin?

(iv) The authors studied the properties of the porphyrins bound to wide band gap semiconductors (TiO₂, ZnO). To what does the term *band gap* refer in these metal oxides, and in what way do the absorbed porphyrins interact with this band gap in DSSCs?

3. (2.0 points) Figures 5 (b), 7 (b), and 8 from the paper are reproduced on the following page, showing (top to bottom) the fluorescence spectra in methanol, the UV-vis spectra on ZnO, and the fluorescence spectra on ZrO₂ for the four tetra(trimethylammonium)-carboxyporphyrin salts. As can be seen, the fluorescence emission spectra of all compounds in methanol are very similar, but the UV-vis spectra of the compounds on ZnO show some marked differences, and the same can be seen among the fluorescence spectra of the compounds on ZrO₂. What reasons do the authors give for the differences that are apparent when the compounds are bound to metal oxide substrates. In particular, what accounts for the ZnO-bound *p*-ZnTCPP-[S] UV-vis and the ZrO₂-bound *p*-ZnTCPP-[S] fluorescence spectra being so different from the spectra of the other compounds. Also, why were the fluorescence spectra obtained from samples bound to ZrO₂ instead of ZnO or TiO₂?

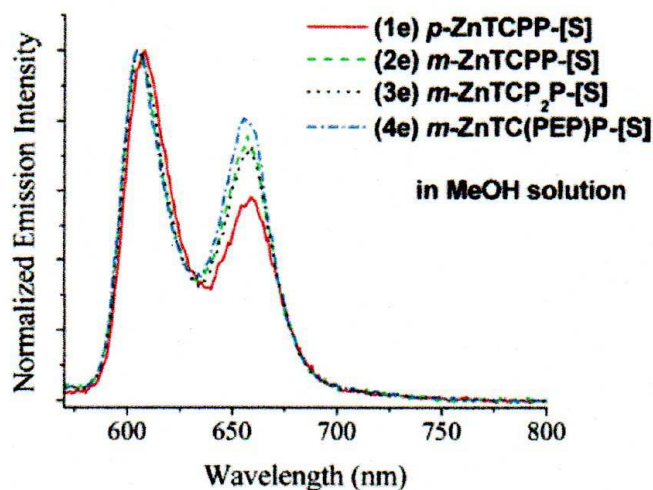


Figure 5 (b). Fluorescence emission spectra of tetra(trimethylammonium)carboxyporphyrin salts recorded in methanol.

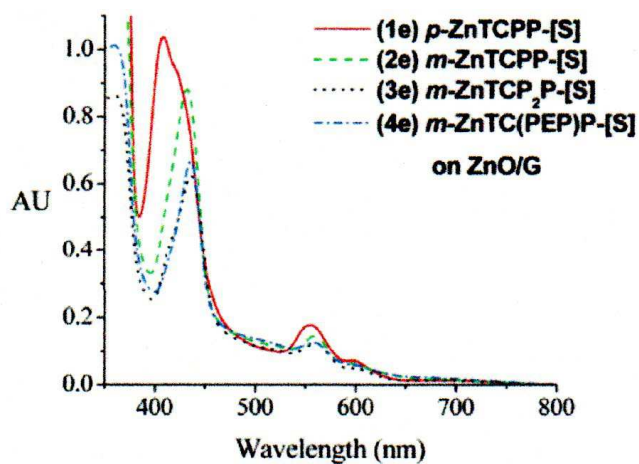


Figure 7 (b). UV-vis absorption spectra of tetra(trimethylammonium)carboxyporphyrin salts on ZnO.

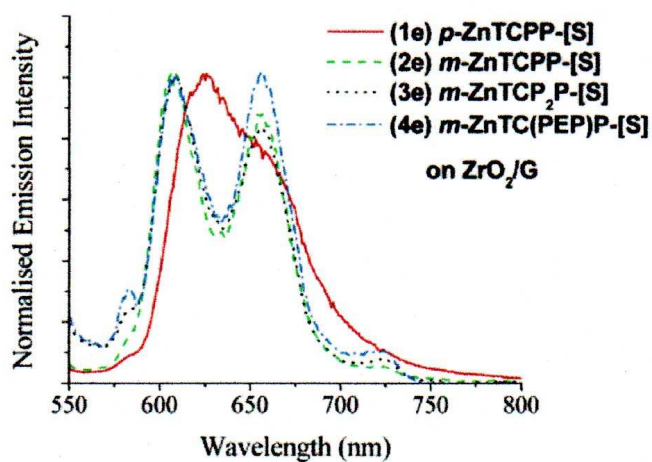


Fig. 8. Fluorescence emission spectra of tetra(trimethylammonium)carboxyporphyrin salts on ZrO₂.

4. (2.0 points) Figure 11, reproduced below, shows plots of incident monochromatic photon-to-current conversion efficiency (IPCE) as a function of wavelength for the ammonium salts, and Table 4, also reproduced below, gives numerical data gleaned from these plots.

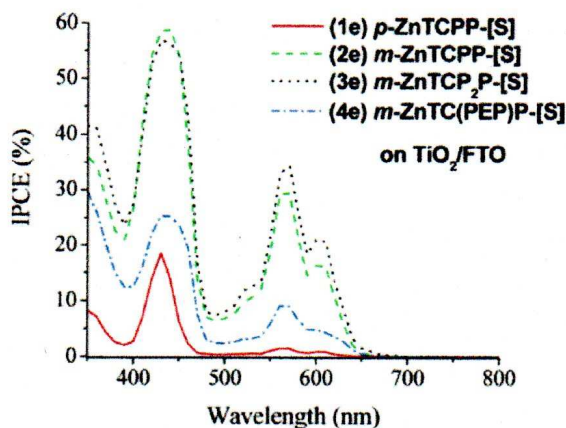


Figure 11. Photocurrent action spectra of tetra(triethylammonium)-carboxy porphyrin salts.

Table 4. Photoelectrochemical Properties of Tetra(triethylammonium)carboxy porphyrin Salts

porphyrin	I_{sc} (mA cm ⁻²)	V_{oc} (V)	ff	IPCE (%)		
				430 nm	570 nm ^a	600 nm ^b
(1e) <i>p</i> -ZnTCPP-[S]	0.39	0.44	0.54	18.50	1.44 (0.08)	0.86 (0.05)
(2e) <i>m</i> -ZnTCPP-[S]	3.33	0.51	0.41	58.60	29.40 (0.50)	16.30 (0.28)
(3e) <i>m</i> -ZnTCP2P-[S]	3.72	0.50	0.42	56.90	34.50 (0.61)	21.10 (0.37)
(4e) <i>m</i> -ZnTC(PEP)P-[S]	1.36	0.43	0.45	25.30	9.00 (0.36)	4.81 (0.19)

^a In parentheses are the Q(1,0) vs Soret peak intensity ratios. ^b In parentheses are the Q(0,0) vs Soret peak intensity ratios.

What do these data tell us about the influence of mode of porphyrin-to-substrate binding and porphyrin-to-substrate distance on the efficiency of these chromophores in DSSCs? What do these results suggest about the mode of photon-to-electron conversion at the molecular level?

Green Chemistry Question (2.0 points) Discuss at some length the importance of work such as this paper to advancing the broader goals of Green Chemistry.