On the energy gap determination for organic semiconducting molecules: the case of porphyrin derivatives

Rian E. Aderne[1], Bruno Gabriel A. L. Borges[2], Harold C. Ávila[3], Liziane Bugalski[4], Fredrik von Kieseritzky[5], Jonas Hellberg[6], Marlus Koehler[7], Marco Cremona[1], Lucimara S. Roman[4,7] C. Moyses Araujo[8,9], Maria Luiza M. Rocco[2], Cleber F. N. Marchiori[8]

[1]Departamento de Física, PUC-Rio, 22453-900, Rio de Janeiro-RJ, Brazil
[2]Instituto de Química, Universidade Federal do Rio de Janeiro-UFRJ, 21941-909, Rio de Janeiro-RJ, Brazil
[3] Department of Physics, University of Atlantic, Puerto Colombia, Atlántico, Colombia
[4]Programa de Pós-Graduação em Engenharia dos Materiais-PIPE, Universidade Federal do Paraná-UFPR, 81531-980, Curitiba-PR, Brazil
[5] Department of Neurobiology, Care Sciences and Society, Karolinska Institutet, Stockholm, Sweden
[6] Chemtronica AB, Bergkällavägen 37C,192 79 Sollentuna, Sweden
[7]Departamento de Física, Universidade Federal do Paraná-UFPR, 81531-980, Curitiba-PR, Brazil
[8]Materials Theory Division, Department of Physics and Astronomy, Uppsala University, Box 516, 75120 Uppsala, Sweden.
[9] Department of Engineering and Physics, Karlstad University, 65188 Karlstad, Sweden

Support information

Ferrocene (Fc/Fc+) voltammogram

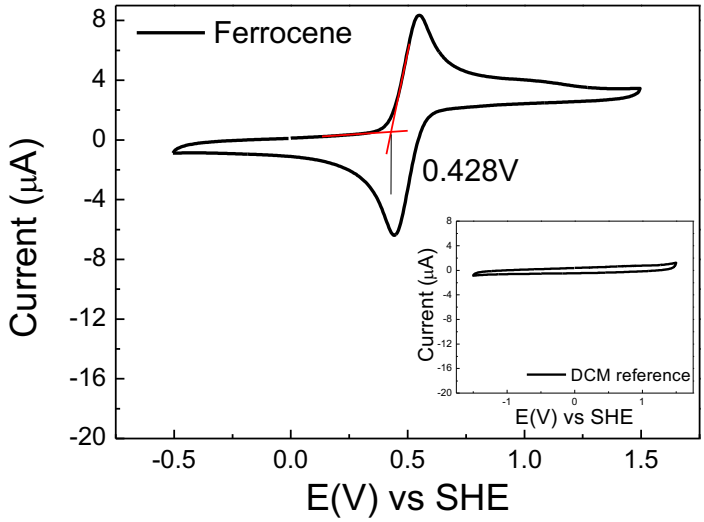

Figure S1 – The characteristic voltammogram of Ferrocene(Fc/Fc+) as reference sample. Two peaks of oxidation and reduction were observed at 0.548 V and 0.445 V, respectively. The potential obtained through the onset methodology is located at 0.428 V. The insert figure shows the solvent DCM voltammogram profile.

The Ionization Potential (IP) and the Electron Affinity (EA) for the compounds were determined from the onset of the oxidation and reduction processes, respectively using the equations 1 and 2, where **e** is the electron charge, and **Fi** is the correction factor

between ferrocene value found in the literature with that observed during the measurements.

$$E_{IP}\,(eV) = e.\,E_{ONSET}^{OXI}\,(V) + 4.8\,(eV) - e.Fi\,(V) \qquad \textbf{(eq.1)}$$

$$E_{EA}\,(eV) = e.\,E_{ONSET}^{RED}\,(V) + 4.8\,(eV) - e.Fi\,(V) \qquad \textbf{(eq.2)}$$

Table S1 – Ionization Potentials, Electron Affinities (EA) and Electrochemical Energy Gap (EE_G) obtained for the three porphyrin derivatives from Cyclic Voltammetry measurements in solution.

	IP (eV)	EA (eV)	Gap (eV)
H_2TTP	-5.28	-3.36	1.92
$H_2$5BrTTP	-5.39	-3.44	1.95
Zn5BrTTP	-5.31	-3.34	1.97

Tauc plot:

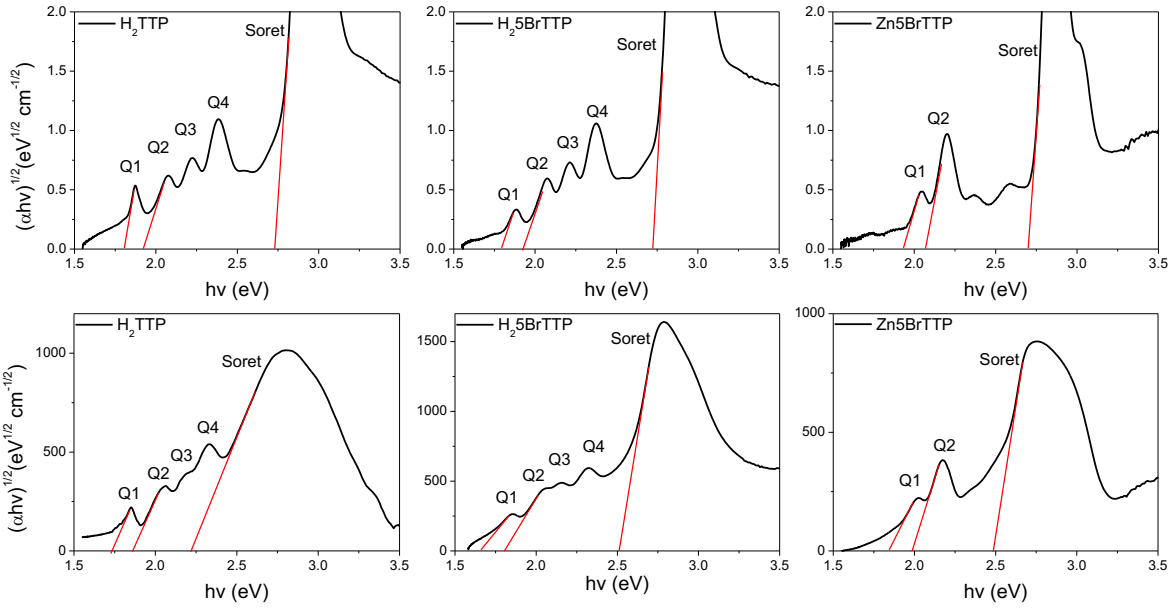

Figure S2 – Tauc plot analysis for UV-Vis spectra of H_2TTP, $H_2$5BrTTP and Zn5BrTTP in solution (first row) and thin film (second row).

Table S2 – Summary of energy levels taken from the Tauc plot and the Onset method. The highlight for the bands Q1 and Q2 were compared with the simulations performed. In addition, comparison between the Soret band and REELS measurements.

	Solution 10^{-5} M in THF			Thin film			
Tauc plot	***Q1***	***Q2***	***S***	***Q1***	***Q2***	***S***	***REELS*** $_{onset}$
	(eV)	***(eV)***	***(eV)***	***(eV)***	***(eV)***	***(eV)***	***(eV)***
H_2TTP	1.81	1.94	2.77	1.77	1.90	2.25	2.45
$H_2$5BrTTP	1.80	1.92	2.72	1.70	1.84	2.51	2.30
Zn5BrTTP	1.85	1.99	2.50	1.86	1.99	2.49	2.37

	Solution 10^{-5} M in THF			Thin film		
Onset	***Q1***	***Q2***	***S***	***Q1***	***Q2***	***S***
	(eV)	***(eV)***	***(eV)***	***(eV)***	***(eV)***	***(eV)***
H_2TTP	1.84	1.99	2.78	1.79	1.95	2.43
$H_2$5BrTTP	1.82	1.98	2.75	1.76	1.92	2.49
Zn5BrTTP	1.97	2.12	2.75	1.85	2.01	2.52

	Solution 10^{-5} M in THF			Thin film		
Inflection point at a slope	***Q1***	***Q2***	***S***	***Q1***	***Q2***	***S***
	(eV)	***(eV)***	***(eV)***	***(eV)***	***(eV)***	***(eV)***
H_2TTP	1.86	2.04	2.90	1.84	1.98	2.62
$H_2$5BrTTP	1.85	2.05	2.84	1.80	1.98	2.62
Zn5BrTTP	2.01	2.17	2.82	1.95	2.09	2.62

	Solution 10^{-5} M in THF			Thin film		
Half the value of the peak	***Q1***	***Q2***	***S***	***Q1***	***Q2***	***S***
	(eV)	***(eV)***	***(eV)***	***(eV)***	***(eV)***	***(eV)***
H_2TTP	1.85	2.03	2.87	1.80	1.98	2.56
$H_2$5BrTTP	1.84	2.02	2.84	1.80	1.99	2.67
Zn5BrTTP	2.00	2.15	2.81	1.97	2.12	2.60

UV-Vis Measurements versus concentration:

UV-Vis measurements were performed in solution for different concentrations, from 10^{-4} M to 10^{-7} M (see Figure S3). It is evident the linear behavior of the absorption intensity as a function of concentration; even at low concentrations there is the formation of the dimer.

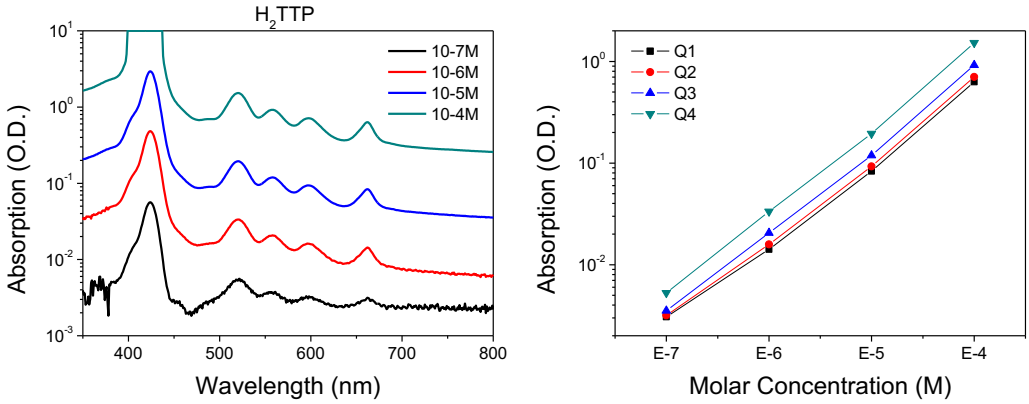

Figure S3 - Absorption spectra of H_2TTP porphyrin ranging from 10^{-4} to 10^{-7} M in THF and the linear behavior of the Q-bands with concentration.