

Supplementary Material

Sensitization of TiO₂ Films by Supramolecular Species Containing Zinc-Porphyrins and Ruthenium Polypyridyl Complexes

Ana F. Nogueira, Luis Fernando O. Furtado, André Luiz B. Formiga, Marcelo
Nakamura, Koiti Araki and Henrique E. Toma^{*}

*Instituto de Química - Universidade de São Paulo. C. P. 26077, CEP 05513-970,
São Paulo – Brazil*

Contents:

Experimental Section

- 1.1. Materials**
- 1.2. Preparation of nanoporous TiO₂ films**
- 1.3. Surface treatment with the dye**
- 1.4. Assembling the cell**
- 1.5. Measurement of the photoelectrochemical properties**
- 1.6. Electronic and emission spectra**
- 1.7. Electrochemical Studies**
- 1.8. Theoretical Calculations**
- 1.9. Scanning Force Microscopy**

References

Experimental Section

1.1. Materials

The synthesis and characterization of TRuphenTPyP, TRubipyTPyP and TRubipyZnTPyP supramolecules were detailed in references.¹⁻³ The TRuphenZnTPyP derivative was obtained by the reaction of the free base species with zinc acetate in methanol. All the counter ions in the supramolecules are TFMS (trifluoromethane sulphonate). Analysis for C₁₄₀H₁₀₀N₂₄Ru₄O₁₈S₄F₁₂Cl₄Zn, exp. (calc.): C = 49,6 (49,8); N = 10.1 (9,9); H = 3,3 (3,0). The TiO₂ powder (P25) was kindly donated by Degussa AG, Frankfurt/M. All others reagent grade chemicals were used without further purification.

1.2. Preparation of nanoporous TiO₂ films

The nanoporous TiO₂ film deposited onto a sheet of F-doped SnO₂ TEC15 conducting glass (sheet resistance $\sim 15 \Omega/\text{cm}^2$) was prepared using a variation of a previously published procedure.⁴ A colloidal TiO₂ suspension was obtained by grinding 6 g of TiO₂ powder in 2 mL of distilled H₂O and 0.2 mL of acetylacetone, in a mortar with a pestle, for about 40 min. Finally 8.0 mL of distilled water and 0.1 mL of Triton X-100 were slowly added with continuous mixing for 10 min.

A previously cleaned conductive glass sheet was laid to a flat surface with the conductive side up and the deposition area was delimited with a plastic adhesive tape. Several drops of the above TiO₂ suspension were spread as evenly possible onto the surface using a glass rod. The thickness of the TiO₂ coating ($\sim 4\mu\text{m}$) was determined by the thickness of the adhesive tape. The electrodes were then dried in air and fired in a furnace, at 450 °C for 30 min.

1.3. Surface treatment with the dye

The electrodes covered by a nanoporous TiO₂ film layer were immersed during 48h in a 1.0×10^{-4} M solution of the TRuphenZnTPyP species in different solvents to achieve the adsorption equilibrium condition. We prepared solutions in ethanol, ethanol/acetonitrile (2:1) and 2,2,2-trifluoroethanol. The surface coverage was roughly estimated by the optical density of the film and color change from white to the color of the attached dye. Afterwards, the electrode was washed with the solvent and dried in moisture-free air.

1.4. Assembling the cell

The cell (1.0 cm^2 active area) was assembled by transferring about 1 mL of the electrolyte solution (0.5M t-butylpyridine, 0.6M tetrabutyl ammonium iodide, 0.1M LiI, 0.1M I_2 in 10 mL methoxypropionitrile) onto the $\text{SnO}_2\text{:F}^-$ glass covered with TiO_2 /attached dye. The counter electrode was then pressed against the TiO_2 /dye film. The transparent counter electrode was treated by transferring a drop of 0.05 mol L^{-1} solution of H_2PtCl_6 in isopropanol onto the conducting glass and firing at $400\text{ }^\circ\text{C}$ in air for 20 min. A PVC film was placed in between the two electrodes to avoid short circuit and electrolyte leakage. The assembly was kept together by a clamp. No further sealing was necessary, at least for the tests described in this communication.

1.5. Measurement of the photoelectrochemical properties

The photoelectrochemical cells (DSSC) were firmly placed in an optical bench for the characterization procedures. The IPCE spectra and the current-voltage (I - V) curve were obtained using an Applied Photophysics 150 W Xenon lamp as a white-light source and a home-made resistor as a variable load. Oriel Spectral Luminator was employed as monochromatic source. The light intensity was varied from 1 to 2 mW cm^{-2} . Measurements of photocurrent and photovoltage were performed using a Keithley 610C electrometer or a calibrated multimeter. The sample was always illuminated through the conducting glass substrate and no corrections were made for the 30 % reflection and transmission losses in the $\text{SnO}_2\text{:F}$ glass. The poly and monochromatic light intensity at the electrode position were measured with a Newport Optical Power Meter model 1830-C.

1.6. Electronic and emission spectra

The UV-vis spectra were obtained in a HP-8453A diode array spectrophotometer in ethanol solution. The emission spectra were recorded on a Photon Technology Inc. model LS100 spectrofluorimeter in N_2 gas saturated ethanol solution.

1.7. Electrochemical Studies

The electrochemistry was carried out in [(C₂H₅)₄N]ClO₄ 0.1 M acetonitrile solution using a potentiostat/galvanostat from Ecochemie, model AUTOLAB PGSTAT30. A conventional three electrode cell consisting of a platinum disk working electrode, Ag|Ag⁺ 0.010 M in acetonitrile ($E^0 = 0.503$ V *vs* NHE) reference electrode and a coiled platinum wire as counter electrode was used.

1.8. Theoretical Calculations

Molecular modeling calculations were carried out for the TRuphenZnTPyP species, starting with the MM⁺ module, a modified MM2 force field⁵ for geometry optimization, within the HyperChemTM program⁶, and using a gradient of 1×10^{-5} kcal Å⁻¹ mol⁻¹ as a convergence criterion in a conjugated gradient method. SCF molecular orbital calculations were performed at the RHF level, using the ZINDO/S method⁷, and the default parameters (and scaling factors $k_{p\sigma} = 1.267$ and $k_{p\pi} = 0.585$). Geometry optimization was refined again, using the atomic charge distribution from the semi-empirical calculations, and the procedure repeated many times, until reaching convergence. The electronic spectrum was calculated, based on single CI excitations in an active space involving 23 frontier molecular orbitals (15 highest occupied and 8 lowest unoccupied MOs). The relevant HOMO and LUMO levels and the fractional orbital mixture are shown in Table 1 while the theoretical and experimental electronic spectra were collected in Table 2.

1.9. Scanning Force Microscopy

For MAC Mode measurements was used PicoSPM I (Molecular Imaging) with MAClever Type II ($k \sim 2,8$ N/m, $f \sim 60$ kHz) operating with Amplitude Setpoint 5.55 V under ambient conditions. The MAC Mode images were obtained with scan rate at 3 Hz and 512 points per line.

Table 1. Molecular orbital energy order and fractional orbital mixing (%) of TRuphenZnTPyP.

Mol. Orbital	Energy / eV	Ru ^{II}	Phen	Cl ⁻	pyridyl	Porphyrin	Zn ^{II}	Water
421	-6.47	4.89	91.69	0.16	2.88	0.38	0.00	0.00
420	-6.47	4.64	91.69	0.16	2.74	0.77	0.00	0.00
419	-6.48	2.29	96.19	0.06	1.23	0.23	0.00	0.00
418	-6.49	2.89	92.09	0.10	3.51	1.41	0.00	0.00
417	-6.50	2.20	95.03	0.05	2.14	0.58	0.00	0.00
416	-6.52	0.60	81.91	0.02	12.36	5.11	0.00	0.00
415	-7.50	0.82	0.47	0.02	10.32	88.35	0.00	0.03
414 (LUMO)	-7.50	0.89	0.52	0.02	10.99	87.54	0.00	0.03
413 (HOMO)	-12.00	38.36	8.14	1.20	11.60	40.48	0.02	0.20
412	-12.20	65.80	25.07	3.68	5.03	0.42	0.00	0.00
411	-12.30	65.58	25.09	3.66	4.96	0.72	0.00	0.00
410	-12.30	65.72	25.22	3.67	4.94	0.45	0.00	0.00
409	-12.30	59.76	28.74	2.16	2.89	6.41	0.00	0.03
408	-12.40	70.03	20.20	1.36	7.72	0.70	0.00	0.00
407	-12.40	69.91	20.18	1.38	7.59	0.94	0.00	0.00
406	-12.40	70.06	20.02	1.30	7.81	0.80	0.00	0.00
405	-12.50	71.13	21.61	5.27	1.58	0.40	0.00	0.00
404	-12.50	71.10	21.73	4.97	2.03	0.17	0.00	0.00
403	-12.50	71.13	21.71	5.47	1.25	0.44	0.00	0.00
402	-12.50	70.89	21.79	4.84	2.23	0.25	0.00	0.00
401	-12.60	0.28	0.09	0.01	1.45	98.17	0.00	0.00
400	-12.70	38.82	9.02	0.41	10.93	40.59	0.01	0.21
399	-13.80	6.28	91.35	1.84	0.48	0.05	0.00	0.00
398	-13.80	6.32	91.30	1.86	0.47	0.05	0.00	0.00
397	-13.80	6.31	91.34	1.83	0.47	0.05	0.00	0.00

Table 2. Selected theoretical electronic transitions of TRuphenZnTPyP.

Observed Band	Theoretical λ / nm	Assignment $MO_i \rightarrow MO_f$	
606, 563	623.9	413 \rightarrow 414; 401 \rightarrow 415	Q ₍₀₋₀₎ , Q ₍₀₋₁₎ band
		413 \rightarrow 415; 401 \rightarrow 414	ibidem
496 sh	483.5	402 \rightarrow 420	Ru \rightarrow phen CT
	476.2	403 \rightarrow 421	ibidem
masked	385.4	410 \rightarrow 415	Ru \rightarrow porphyrin CT
	384.8	412 \rightarrow 415	ibidem
	383.8	412 \rightarrow 414; 411 \rightarrow 414	ibidem
	382.2	408 \rightarrow 414	ibidem
	361.4	406 \rightarrow 414	ibidem
430	339.0	401 \rightarrow 415; 400 \rightarrow 414	Soret band
		401 \rightarrow 414; 400 \rightarrow 415	ibidem

sh = shoulder.

References

- (1) Araki, K.; Toma, H. E.; *J. Coord. Chem.* **1993**, 30, 9.
- (2) Araki, K.; Toma, H. E.; *J. Photochem. Photobiol. A: Chem.* **1994**, 83, 245.
- (3) Araki, K.; Araujo, A. L.; Toyama, M. M.; Franco, M.; Azevedo, C. M. N.; Agnes, L.; Toma, H. E.; *J. Porphyr. Phtalocyanines.* **1998**, 2, 467.
- (4) Nazeeruddin, M.K.; Kay, A.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vanchopoulos, N.; Gratzel, M.; *J. Am. Chem. Soc.* **1993**, 115, 6382.
- (5) Allinger, N. L.; *J. Am. Chem. Soc.* **1977**, 99, 8127.
- (6) HyperChemTM version 6.01 for WindowsTM (Hypercube Inc. Gainesville, FL, USA, 2000)
- (7) (a) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T.; *J. Am. Chem. Soc.* **1980**, 102, 589. (b) Bacon, A. D.; Zerner, M. C.; *Theoret. Chim. Acta* **1979**, 53, 21. (c) Ridley, N.

L.; Zerner, M. C.; *Theoret. Chim. Acta* **1976**, 42, 223. (d) Ridley, N. L.; Zerner, M. C.; *Theoret. Chim. Acta*, **1973**, 32, 111.