Inorganica Chimica Acta, 90 (1984) 221–224

Effect of Axially Coordinated Pi-Acid Ligands on Photovoltaic Properties of Zn-Tetraphenylporphyrin*

COOPER H. LANGFORD**, STEPHEN SETO

Department of Chemistry, Concordia University, 1455 de Maisonneuve Blvd. W., Montreal, Que., H3G 1 MB, Canada

and BRYAN R. HOLLEBONE

Department of Chemistry, Carleton University, Ottawa, Ont. K1S 5B6, Canada

Received March 21, 1984

Following our earlier observations that the well known doping effect of oxygen and water on electrical properties of porphyrin and phthalocyanine films may be attributed to a pi-acid axial interaction throughout the film in the case of PdTPP, we have compared Zn–TPP films supported on transparent n-doped SnO_2 electrodes which had been treated with several pi-acids in contact with an electrolyte to give photoelectrochemical cells. Photovoltages obtained in contact with a series of solution couples were used to obtain approximate photo flat band potentials. The doped films were examined by magnetic circular dichroism (MCD) spectroscopy so that the electronic effect of the dopant could be diagnosed. It was found that pi-acid dopants cause shifts to low energy in the band which indicates "hole stabilization" in the order pyridine < CO < triphenylarsine. The potentials of zero photopotential, 'E_{FB}', correlate approximately with spectral shifts. It is concluded that manipulation of axial ligand dopants is a promising method for design of metal porphyrin and perhaps phthalocyanine films with desired photovoltaic properties.

Introduction

Many papers [*e.g.* 1, 2] have pointed out the importance of oxygen and water doping to the photoelectrochemical properties of porphyrin and phthalocyanine film photovoltaic and photoelectrochemical devices. We have undertaken a program using magnetic circular dichroism (MCD) spectroscopy to try to understand the basis of photoelectrochemical properties of such films [3, 4]. We were fortunate to study palladium tetraphenylporphyrin (PdTPP) where parallel crystalline and amorphous films could be prepared by alternate procedures. The MCD spectra readily revealed the electronic differences between crystalline and amorphous films but the differences did not extend to the photovoltages. On the other hand, photovoltages in both types of film responded to O_2 doping and the changes could be correlated with shifts in the region of the TPP MCD spectrum assigned to axial pi-acid perturbation [5]. We suggested that the axial ligand may affect the energetics of holes in the film.

The obvious next question is the generality of pi-acid effects. In the literature, O_2 and H_2O have been the main dopants but our proposals [4] concerning the doping mechanism suggest a number of other possibilities. In this note we report on electrodes fabricated by coating films of zinc tetraphenylporphyrin (ZnTPP) on a n-doped SnO_2 coated glass (an optically transparent electrode). The films were doped with O_2 (plus H_2O) by exposure to the laboratory atmosphere or with CO, pyridine, or triphenylarsine by additions to the solutions from which the films were cast.

Experimental

Materials

Zinc tetraphenylporphyrin (ZnTPP) was purchased from Eastman Organic Chemicals and purified conventionally. It was confirmed by the absorption spectrum. Common electrolytes used in solution couples were reagent grade materials used without additional purification. The doping agents were CO from a Union Carbide lecture bottle, triphenylarsine (Aldrich), and reagent grade pyridine purified by distillation and dried over $MgSO_4$. Distilled water was purified by a Barnsted RO unit. CH_2Cl_2 was spectrograde dried.

Solutions for electrode preparation consisted of 75 mg of ZnTPP dissolved in 10 ml dry CH_2Cl_2. Doped films were prepared from solutions as follows: (a) 450 mg of triphenylarsine (TPA) added to the ZnTPP/CH_2Cl_2 solution to give a ratio of 6:1 in favour of dopant; (b) saturation of ZnTPP/CH_2Cl_2 solution with CO; (c) use of 10 ml of pyridine (py) to replace CH_2Cl_2 as a solvent for ZnTPP. The mo-

---

*Support under a strategic grant from NSERC Canada is acknowledged.

**Author to whom correspondence should be addressed.

0020-1693/84/$3.00

difications of ZnTPP so achieved are demonstrated spectroscopically. CO does not add to ZnTPP in solution.

Electrode blanks were fabricated from discs of n-doped SnO_2 coated glass, manufactured by Corning and marketed by Johns' Scientific as 'IR Reflective Glass'. Its resistance is ~80 ohm. These are referred to below as optically transparent electrodes (OTE's).

The supporting electrolyte used in all experiments was 1.00 *M* KCl buffered at pH 5.6 with phosphate buffer.

Apparatus and Procedures

Electrodes were prepared as follows. The OTE was cleaned with successive washings with HNO_3, distilled water, and acetone. OTE's not in use were stored in absolute ethanol. Films of doped or undoped ZnTPP were prepared by placing the OTE on the platform of a spin coating device which allowed rotation at about 2,000 rpm for 15 s. Three drops of dye solution was placed on the OTE for 20 s then it was spun. This resulted in a fairly uniform film as judged by optical transmittance. Film thickness (judged as before from absorptivity [3]) was between 500 and 1000 Å. The validity of the absorbance derived values was confirmed by direct measurement in one or two cases. The method did not permit fabrication of uniform films differing much in thickness. This conclusion was reached after experimentation with all the relevant variables. The dye coated OTE was transferred and mounted onto a flow-through cell with the film facing the electrolyte chamber and sealed by pressure with a rubber O-ring and silicone grease. A copper ring was pressed to the dye side of the OTE outside the O-ring. Dye was removed so that the copper contact was directly to n-SnO_2.

Photoelectrochemical measurements were carried out in a three chamber Teflon flow through cell. The circular central chamber (4 mm deep) had an 11 mm diameter window onto which the OTE was pressed (volume ~2 ml). The two cylindrical side chambers were used for a Pt foil counter electrode and a saturated calomel reference electrode (SCE). Solution was circulated at 20 ml/min from a reservoir (which could be used for deoxygenation) using a peristaltic pump and tygon tubing. The dark voltages were measured on Pt with respect to the SCE using a Metrohm EA412 and open circuit photovoltages with a Keithley electrometer with respect to the Pt counter electrode.

Irradiations were carried out with a 300 W tungsten filament lamp filtered through a yellow filter to cut off wavelengths shorter than 470 nm. (The IR reflective character of SnO_2 limits the exposure to IR).

MCD spectra were recorded by mounting the OTE directly in the cylindrical cell holder of the MCD spectrometer. The spectrometer is of local fabrication. Its structure has been described [6]. It should be stressed that OTE's examined do not yield MCD spectra or absorbtion spectra of a quality comparable to porphyrin films on quartz plates found in the literature. This is presumably a consequence of the optical properties of SnO_2. Absorption spectra were recorded using a Perkin-Elmer 322.

Results and Discussion

Photoelectrochemistry

Electrolyte components were introduced into the supporting electrolyte at 2 m*M* concentrations and solution was circulated until potentials were stable. The couples studied (with their observed dark potentials in V referred to the normal hydrogen electrode followed by their *standard* potentials in V in parentheses) are as follows: (1) *o*-quinone/hydroquinone (0.365, 0.369); (2) I_3^-/KI (0.630, 0.536); (3) Sn^{4+}/Sn^{2+} sulfate (0.220, 0.150); (4) $K_2S_2O_3$ (0.490, 0.40); (5) UO_2 nitrate (0.420, 0.33); (6) H_3AsO_3 (0.460, 0.56); (7) Fe(II) EDTA (0. 264); (8) potassium $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ (0.40, 0.36). Figure 1 shows photovoltages plotted against dark potentials for various couples in contact with the various doped films. The film marked 'O_2' doped in simply a film that has been equilibrated with the laboratory atmosphere prior to mounting. In the context of earlier experience [1, 4], this should be more precisely described and O_2/H_2O doped. (The precise mechanism is not clear but may well involve peroxide.)

To a reasonable approximation the photovoltages observed are linearly related to the dark potentials.

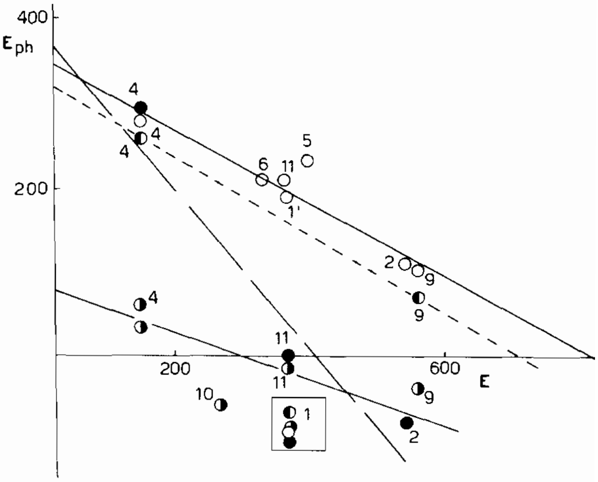

Fig. 1. Plot of open circuit photovoltage in millivolts (Eph) against the dark voltage referenced to NHE in millivols (E). The reference numbers for the redox couples are those given in the results section of the text. The circles have the following significance: ○ oxygen doped; ● TPA doped; ◑ CO doped; ◐ pyridine doped.

It is possible to estimate intercepts which give solution potentials where the photovoltages go to zero. There are: 'O_2', +0.82 V; py, +0.70 V; $(C_6H_5)_3As$, +0.40 V; CO, +0.29 V. Note that the value for CO establishes, that the CO 'doping' effect is not reversible when the electrode dries. This is surprising but supported by MCD. The values of these intercepts should provide a useful approximation to the flat band photo potential, E_{FB}, for each electrode.

The case of quinone–hydroquinone does not fit the linear correlations. The point for this couple is very nearly the same after steady state is reached on all films. The steady state is, however, reached slowly. The point marked 1′ is an *initial* value on the 'O_2, doped film. It is seen to be very close to the correlation line. The explanation is most probably that components of this couple are specifically adsorbed into the ZnTPP film and participate as dopants. This is of some general significance since this electrolyte is commonly used as a reference couple for porphyrin electrodes.

The electrolyte–porphyrin–SnO_2 electrode has two potentially photochemically active interfaces, the one between SnO_2 and the film and the interface with the electrolyte. Since these porphyrin materials have p-type semiconducting behaviour [1, 2] the photoeffects are probably related to electron (minority carrier) photoprocesses. As before [4], cathodic photoprocesses would be attributed to transfer of photoelectrons to the solutions (as in the case of quinones). The anodic processes result from transfer of photoelectrons to the SnO_2 semiconducting support which is the locus of the adsorption of photons entering through the glass. The reaction with the electrolyte depends on the holes at the interface and the variations in photovoltage measure the *hole* levels in the doped films. Fig. 2 shows a proposed hole energy level scheme based on these estimated flat band potentials.

Previous attempts to manipulate photopotentials on porphyrins or phthalocyanines in electrochemical or 'catalytic' systems have focussed on variation of the central metal, solvent and ring substituents (see *e.g.* [7]). Variations of a similar magnitude are also readily available by manipulation of dopants. Given the earlier evidence [4], for a molecular 'hopping' conduction mechanism, this is especially interesting in terms of attachment of porphyrins to electrodes *via* surface or polymer bound ligands with pi acid character.

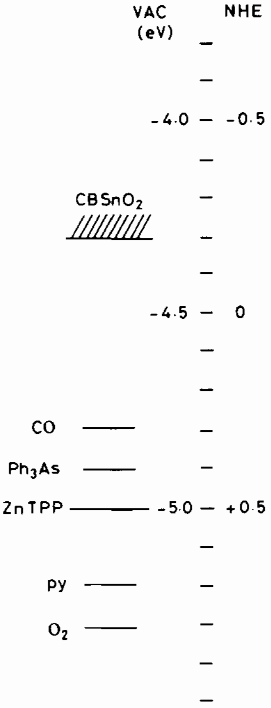

Fig. 2. Hole energy levels for films with various dopants refered to the work function of ZnTPP at −5.0 eV in vacuum or +0.5 V on the NHE scale. The level of the tin oxide conduction band is shown at the top of the diagram.

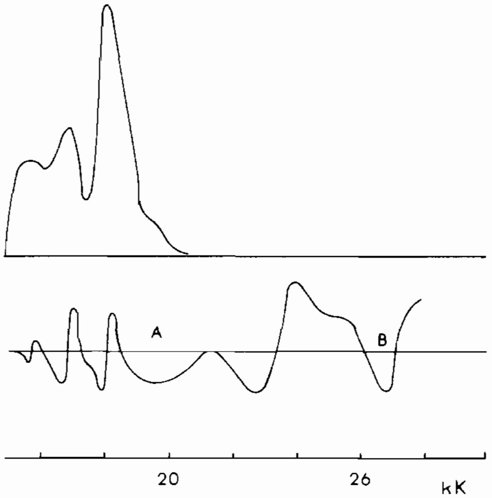

Fig. 3. The absorption (top) and MCD spectra (bottom) of a CO doped ZnTPP film on tin oxide coated glass. The energy axis is in thousands of wave numbers (kilokysers). The dichroism axis is in arbitrary units.

Spectroscopy

In Figs. 3 and 4 the adsorption and MCD spectra of CO and TPA doped ZnTPP films on OTE's are shown. Data for the remaining cases are collected in Table I. The spectra bear resemblances to those of ZnTPP with axial ligands [5, 8] but are more complex than solution spectra because of Davydov interactions similar to those observed in phthalocyanine films [9]. The absorption data span the visible region while the MCD are available to shorter wavelength because of the greater dynamic range of the MCD instrument. In these films the upper energy limit for MCD was 28,000 cm^{-1}.

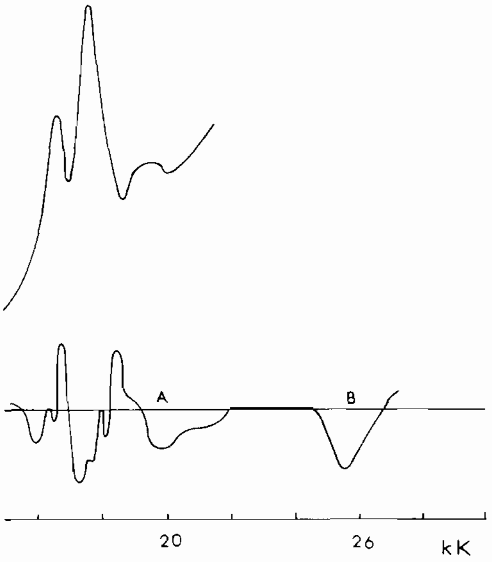

Fig. 4. The absorption (top) and MCD (bottom) spectra of a triphenylphosphine doped ZnTPP film on tin oxide coated glass. Presnetaion is as in Fig. 3.

The spectra can be assigned for D_{4h} symmetry [9]. The α, and Soret bands are all $'A_{1g} \rightarrow$ 'Eu from $(\pi \rightarrow \pi^*)$ configurations $(a_{2u} \rightarrow e_g)$ $(a_{1u} \rightarrow e_g)$ and $(b_{2u} \rightarrow e_g)$ respectively.

The side band on the two allowed visible transitions, marked "A" in Figs. 3 and 4 occurs in all axial ligand derivatives with a B term of variable sign in the MCD. It is a vibronic transition $'A_{1g} \rightarrow 'A_{2a}$ from coupling of the e_u vibration with the e_g π^* orbital. On the high energy side of the Soret is a band marked 'B', assigned as $'A_{1g} \rightarrow 'A_{2g}$ from the configuration $b_{2g} \rightarrow b_{1g}$ (π^*) [9]. The b_{1u} (π^*) has amplitude at the donor N atoms and may interact strongly with axial ligand orbitals. The transition is red shifted by stabilization of the orbital by π acids. It will also interact with the vibronic transition since both excited states have A_2 symmetry. As band 'B' is red shifted towards band 'A' in the sequence py < CO < TPA the MCD signal at the Soret weakens until band 'B' appears as the first UV band in the TPA complex. In the same sequence, the MCD sign of band 'A' reverses from positive to negative at the CO derivative (Fig. 3) and the vibronic interval increases from 1100 to 1300 cm^{-1} in the TPA derivative (Fig. 4). All this suggests that in the TPA complex the interaction between $'A_{2u}$ states is very strong and that the ligand π acidity has strengthened the in-plane bonding by removal of π^* density on the d^{10} metal ion [5].

Correlation of Photovoltages with Spectra

For all complexes except the TPA derivative the photovoltage intercept decreases (Fig. 1) as the UV bands are red shifted. The intercept for the TPA complex is high but the slope is much greater suggesting a different mechanism. This correlates with the appearance of the $n \rightarrow \pi^*$ transition as the first UV band in the MCD spectrum. Together these suggest the creation of a non-bonding type of hole rather than the bond hole in the film observed with weaker π acid axial ligands. Thus a new photomechanism appears to be possible with very strong π acid ligands. More such synergic structures may be predicted from an analysis of available ligand orbitals [10].

References

1 F. R. Fan and L. R. Faulkner, *J. Am. Chem. Soc., 100,* 4279 (1978).

2 S. C. Dahlberg in J. S. Connely, ed., 'Photochemical Conversion and Storage of Solar Energy', Academic Press, N.Y., 1981, p. 407.

3 C. H. Langford, B. R. Hollebone and T. Vandernoot, *Adv. Chem. Ser., 184,* 139 (1980).

4 C. H. Langford, B. R. Hollebone and D. Nadezhdin, *Can. J. Chem., 59,* 652 (1981).

5 M. Nappa and J. S. Valentine, *J. Am. Chem. Soc., 100,* 5075 (1978).

6 E. R. Zygowicz, B. R. Hollebone and H. M. Perkins, *Clin. Chem., 26,* 1413 (1980).

7 A. P. B. Lever and P. C. Minor, *Adv. Mol. Relax. Processes, 18,* 115 (1980).

8 W. R. Browett and M. J. Stillman, *Inorg. Chim. Acta, 49,* 68 (1981).

9 B. R. Hollebone and M. J. Stillman, *J. Chem. Soc. Far. II, 74,* 2107 (1978).

10 B. R. Hollebone, *J. Chem. Soc. (A),* 3104 (1971).

TABLE I. Band Centres and Types for ZnTPP Derivative Films.

Axial ligands	α		β		'A'		Soret		'B'	
	Centre[a]	Type	Centre[a]	Type	Centre[a]	Type	Centre[a]	Type	Centre[a]	Type
O_2	17.0	A	18.2	A	19.3	+B	23.2	A	26.8	−B
PY	16.8	A	18.0	A	19.4	+B	23.2	A	26.8	−B
CO	16.8	A	18.1	A	19.8	−B	23.4	A	26.6	−B
TPA	16.5	A	18.0	A	19.9	−B	[b]		25.6	−B

[a] In units $cm^{-1} \times 10^{-3}$ (kK). [b] Two very weak A terms remain at approximately 24.0 and 25.0×10^3 cm^{-1} which are at least one order of magnitude less intense than in solution (see Fig. 4).