

Figure 2 Cyclic voltammogram of annealed MgPc film in aqueous 1 M KCl solution.

of an irreversible path in the film [1]. In contrast with the difference in the first oxidation potentials, the as-deposited and the annealed MgPc behaved in similar manners for the subsequent redox cycling, i.e., they showed reduction and oxidation potentials of  $-0.40$  and  $+0.60$  V (versus SCE), respectively (see Fig. 2 and [1]).

The as-deposited MgPc film has an intense absorption maximum at around  $685$  nm with a shoulder at around  $650$  nm. After the oxidation, the bluish film changed to purple, since the  $685$  nm peak decreased and the  $550$  nm peak grew. After the first oxidation reduction cycling, the absorption spectrum recovered to that of the virgin film (Fig. 3, curve  $a_3$ ). Similar spectral features of the as-deposited MgPc have been reported elsewhere [1].

The absorption spectrum of the annealed film

(Fig. 3, curve  $b_1$ ) is red shifted and broadened compared with that of the virgin MgPc. The absorption of the metal phthalocyanines has been recognized to shift toward a longer-wavelength region by heat treatment [6]. A slight change in the absorption spectrum or a colour change in the heat-treated film is seen after the first oxidation. In contrast, after the first oxidation reduction cycling (Fig. 3, curve  $b_3$ ), the film showed a similar absorption spectrum to that of the as-deposited MgPc (Fig. 3, curve  $a_3$ ).

Fig. 4 shows FTIR absorption spectra for the as-deposited and the annealed samples, together with the results after the first oxidation and the first oxidation-reduction. Typical absorption lines cited in the text are listed in Table I, where the numbering system of Sidorov and Kotlyar [3] is adopted. Absorption line 8 of the virgin film ( $774\text{ cm}^{-1}$ ), characteristic of the  $\alpha$ -phase, disappears and a new absorption line 9 ( $780\text{ cm}^{-1}$ ) appears after heat treatment. This resulted from the  $\alpha \rightarrow \beta$  transition of MgPc [3, 10]. Doublets are seen for lines 20 and 28 of the annealed film. The appearance of these doublets are also peculiar to  $\beta$ -MgPc [10, 11]. Absorption line 20 and line 28 become a single line after the first oxidation, indicating that the oxidation of  $\beta$ -MgPc induces a structural transition other than  $\beta$ . Absorption line 8 of annealed MgPc ( $780\text{ cm}^{-1}$ ) is unchanged after the first oxidation and shifts to  $774\text{ cm}^{-1}$  of the  $\alpha$  polymorph after the first oxidation reduction. The result is consistent with that of the visible absorption mentioned already. Absorption line 18 ( $1078\text{ cm}^{-1}$ ) of the as-deposited film is attributed to C-N stretching vibration of the

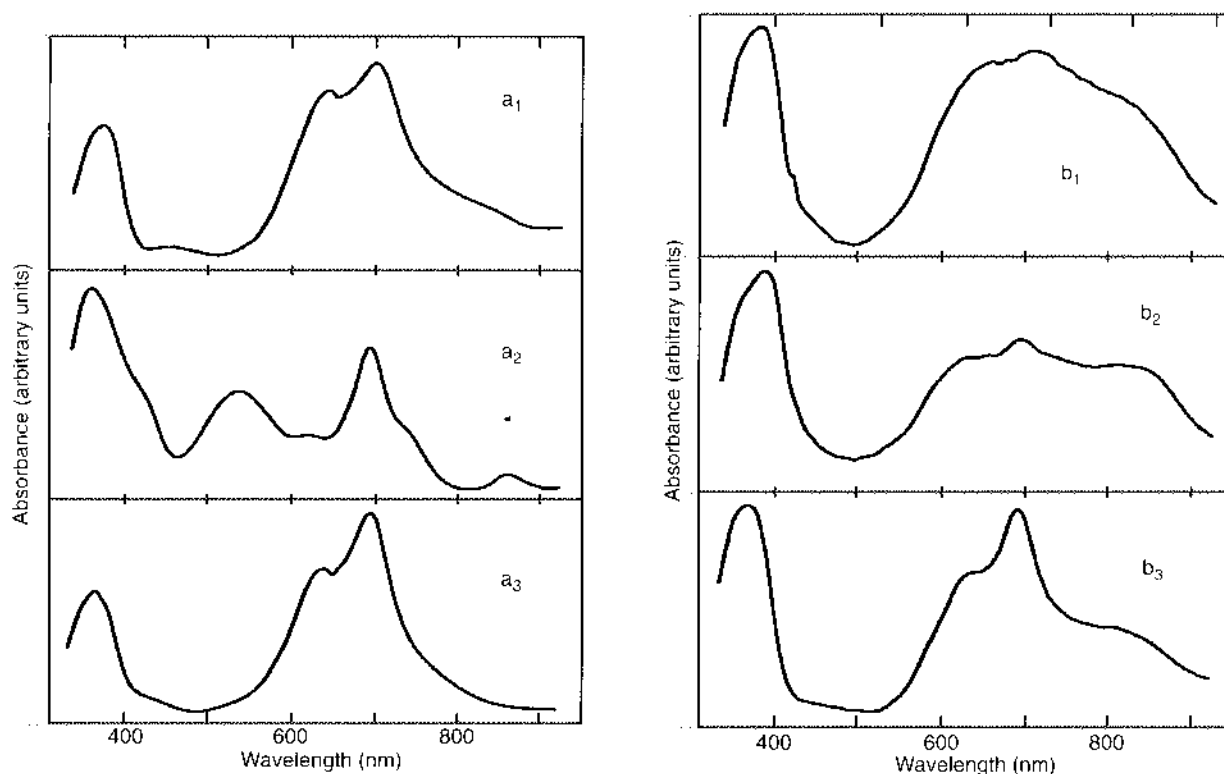


Figure 3 Visible absorption spectra of as-deposited and annealed MgPc films: curve  $a_1$ , as deposited; curve  $a_2$ , as deposited, after the first oxidation; curve  $a_3$ , as deposited, after the first oxidation-reduction; curve  $b_1$ , annealed; curve  $b_2$ , annealed, after the first oxidation; curve  $b_3$ , annealed, after the first oxidation-reduction.

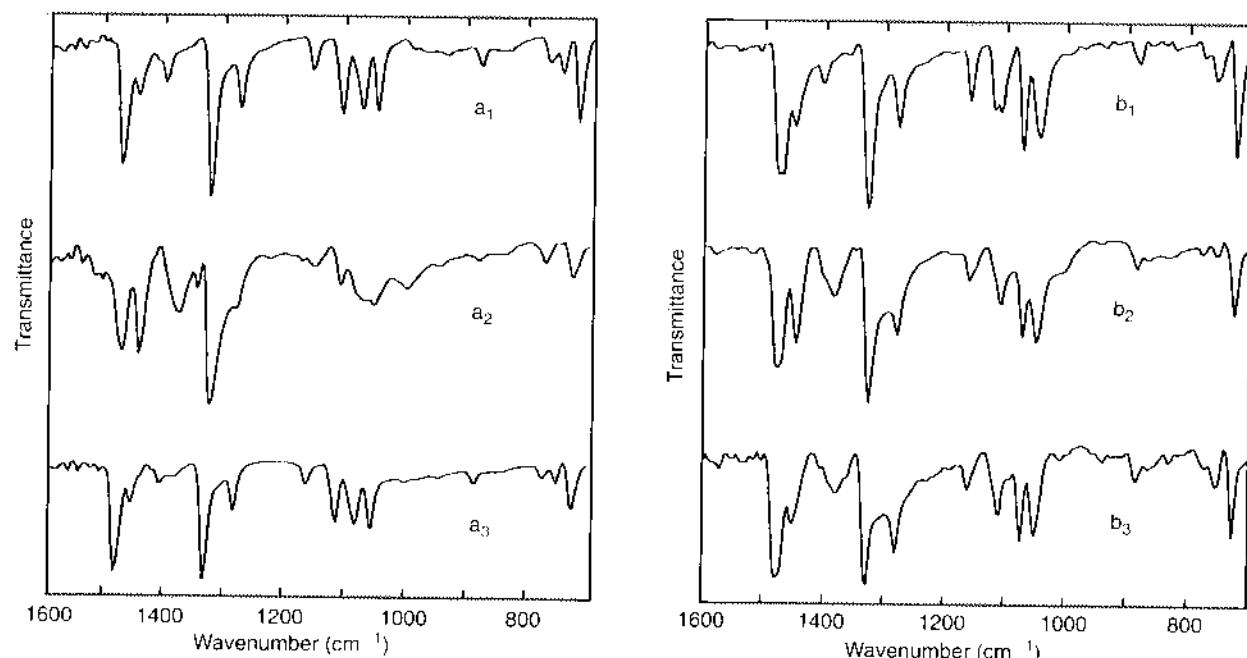


Figure 4. FTIR spectra of as-deposited and annealed MgPc films: curve  $a_1$ , as deposited; curve  $a_2$ , as deposited, after the first oxidation; curve  $a_3$ , as deposited, after the first oxidation-reduction; curve  $b_1$ , annealed; curve  $b_2$ , annealed, after the first oxidation; curve  $b_3$ , annealed, after the first oxidation-reduction.

TABLE 1. FTIR absorption lines cited in the text

Absorption line	Wavenumber (cm <sup>-1</sup> )					
	As-deposited MgPc			Annealed MgPc		
	As-deposited	After first oxidation	After first oxidation-reduction	Annealed	After first oxidation	After first oxidation-reduction
8	774	775	774			774
9				780	781	—
18	1092	1074	1084	—	1078	1076
20	1115	1115	1115	1114	1113	1113
28	1456	1447	1456	1425		
				1452	1447	1452
				1472		

MgPc molecule [10] and is related to the colour change of the film. Absorption line 18 of the virgin film shifts toward a lower-energy region after the first oxidation and recovers to that of the as-deposited after the first oxidation-reduction. As for the annealed film, absorption line 18 scarcely changed for redox cycling, which also agrees with the result of the visible absorption of this film.

In summary the following results are obtained.

1. The potential barriers for anions to migrate through MgPc films at the first oxidation is higher in  $\beta$ -phase films than in  $\alpha$ -phase films.

2. Stretching of carbon-nitrogen bonds in the phthalocyanine rings causes the electrochromism, or the reversible colour change, of MgPc. Oxidation of as-deposited ( $\alpha$ -phase) films leads to a change in colour from blue to purple while that of the heat-treated ( $\beta$ -phase) films does not lead to any colour change.

3. Oxidation of  $\beta$ -phase films induces structural transformation to a phase other than  $\beta$ .

### Acknowledgement

The authors thank Mr W. Gouda for his assistance with the FTIR measurements.

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*Received 21 April  
and accepted 19 August 1997*