Gas-sensing Properties of Semiconducting Films of Crown-ether-substituted Phthalocyanines

Philippe Roisin,[a] **John D. Wright*,**[a] **Roeland J. M. Nolte,**[b] **Otto E. Sielcken**[b] **and Stephen C. Thorpe**[c]

[a] *Centre for Materials Research, University Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH, UK*
[b] *Department of Organic Chemistry, University of Nijmegen, 6525 ED Nijmegen, The Netherlands*
[c] *Health and Safety Executive, Broad Lane, Sheffield S3 7HQ, UK*

The effects of nitrogen dioxide and ammonia on the semiconductivity properties of solution-deposited thin films of the tetra-substituted 15-crown-5, 18-crown-6 and 21-crown-7 metal-free and copper phthalocyanines are reported. The 15-crown-5 films showed good reversible conductivity changes at room temperature in NO_2 concentrations up to 5 ppm. The sensor characteristics worsen as the size of the crown-ether ring increases and this is consistent with the effect of greater separation of adjacent adsorbed species as molecular size increases. Lateral repulsions, which are believed to play a dominant role in controlling the response and reversal processes, are reduced by this increase. Treatment of the films with aqueous KCl solution led to dramatic changes in gas-sensing properties and, for the 15-crown-5 derivative, in film morphology. After KCl treatment the film conductivity decreased very rapidly and reversibly on exposure to NO_2, even at room temperature, and the 15-crown-5 film changed from a polycrystalline needle structure to an extremely smooth structure. These effects are tentatively ascribed to pronounced changes in the molecular assembly induced by the interaction of the potassium ions with the crown-ether moieties, and to consequent changes in the porosity of the film to small gas molecules. Above 3 ppm NO_2 the response begins to saturate, suggesting depletive chemisorption on an n-type material. However, similar responses are also observed for the electron-donor gas ammonia, indicating the presence of both donor and acceptor impurities in the materials. The gas-sensing properties of the KCl treated films at room temperature are the best of any organic semiconductor film yet reported.

Keywords: *Phthalocyanine; Crown-ether; Nitrogen dioxide; Semiconductivity; Gas sensor*

The semiconductivity of phthalocyanine films is strongly increased in the presence of adsorbed electron-acceptor gases. This effect is due to charge transfer between the electron-donating phthalocyanine molecules and the electron-accepting gas, which has been shown to reduce the activation energy for charge-carrier generation, and it has been studied widely in recent years with the objective of producing a new generation of gas sensors.[1] Although the sensitivity of devices based on sublimed films of conventional metal–phthalocyanine complexes is excellent, offering detection of NO_2 down to ppb levels, for example, the response rate and reversibility of such devices is generally lower than the optimum for a practical sensing device. The latter properties appear to be influenced by both the chemical and physical structure of the films,[1] and although there are numerous reports in the literature of attempts to optimise these structures, very little success has been achieved in producing materials which respond and reverse rapidly at room temperature. However, recently a series of phthalocyanines with four crown-ether rings attached has been synthesized[2] (Fig. 1), and it seemed likely that these materials might show interesting gas-sensor properties since the crown-ether groups can act both as spacers, providing control over the lateral separation of neighbouring phthalocyanine molecules, and as functional groups capable of promoting better molecular assembly within the films. The variable size of the non-conjugated and relatively low-polarisability crown-ether groups permits controlled variation of the separation between adsorption sites for electron-acceptor molecules on the surface of films of the materials, as well as systematic variation in the polarisability of the material immediately surrounding an adsorption site. Such variations are expected to have a significant effect on gas adsorption and hence on gas-sensing properties of the films, as will be

a: M = 2H, n = 0
b: M = 2H, n = 1
c: M = 2H, n = 2
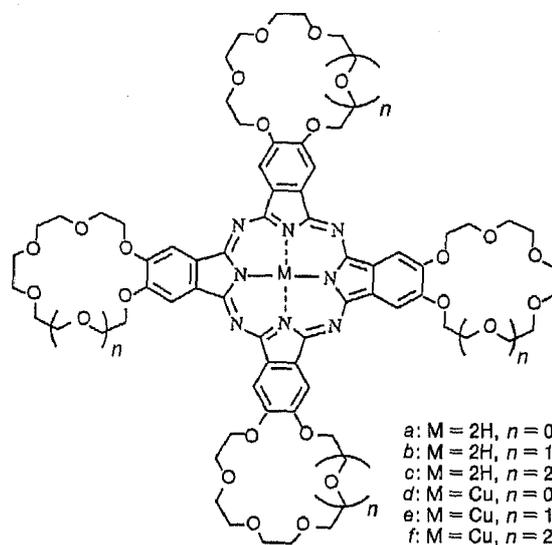d: M = Cu, n = 0
e: M = Cu, n = 1
f: M = Cu, n = 2

Fig. 1 Crown-ether-substituted phthalocyanines

discussed later. Treatment of these materials with alkali-metal ions has been shown to influence the way in which the molecules assemble to form solid films.[2] Such ions would therefore provide the opportunity both to improve the structural ordering of the films and to block the empty spaces in the centres of the crown-ether moieties which would otherwise provide potential channels for diffusion of small gas molecules into the bulk of the film. We now report the first studies of gas-sensing properties of the films of such materials, which confirm the strong effect of alkali-metal ions and show that

these films have unique properties of very fast response and reversal to NO_2 at room temperature.

Experimental

Materials

4,5,4′,5′,4″,5″,4‴,5‴-Tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyanine **(1a)**, 4,5,4′,5′,4″,5″,4‴,5‴-Tetrakis(1,4,7,10,13,16-hexaoxahexadecamethylene)phthalocyanine **(1b)**, and 4,5,4′,5′,4″,5″,4‴,5‴-Tetrakis(1,4,7,10,13,16,19-heptaoxanonadecamethylene) phthalocyanine **(1c)** and their copper complexes **(1d–f)** were prepared from the corresponding benzo crown ethers by conversion to the dicyanobenzo crown ethers (by bromination and treatment with CuCN) and cyclisation.[2] Purification was effected by column chromatography on neutral alumina with chloroform–methanol (10 : 1 v/v).

Films were deposited on alumina substrates fitted with interdigitated platinum electrodes, with integral platinum heaters, by spreading a concentrated solution of the material in chloroform over the substrate with a Pasteur pipette and allowing the solvent to evaporate slowly in a closed chamber which also contained a small amount of chloroform in a beaker. With practice it was found possible to obtain uniform films in this way, although little control of film thickness was possible.

For some measurements these films were subsequently treated with 1 drop of an aqueous solution containing 1 g dm⁻³ KCl, again leaving the films in a closed chamber until the solvent had evaporated, typically within 2 h at room temperature. Although the materials are not water-soluble, it was observed that the drop of KCl solution became coloured after some time, particularly for the 15-crown-5 derivative, suggesting substantial interactions between the ions and the molecule and possibly surface reconstruction by a dissolution mechanism.

Methods

The films were examined using a Cambridge Stereoscan 250 Scanning Electron Microscope operated at either 6.8–7 or 20 keV. Charging effects were avoided by earthing the interdigitated electrodes of the substrate, and it was not necessary to metallise the films.

Electrical conductivity measurements were made in various gas atmospheres using a computer-controlled test rig. Two mass-flow controllers were used, one controlling the flow of clean dry air produced via a Signal AS80 air purifier and the second controlling the flow from a cylinder containing a standard gas mixture (8 ppm for NO_2 and 100 ppm for ammonia) supplied by British Oxygen Company Special Gases Division. The total volume flow was maintained constant by computer control, with the gas concentration determined by the mixing ratio of the two gas streams. For studies of reversal of the gas effects in clean air, a solenoid valve provided a flow of clean air only over the sample. The d.c. conductivities of the phthalocyanine films were measured using a battery-powered voltage source and an electrometer interfaced to the microcomputer to permit current readings as a function of time. Since many of the films had high resistance at room temperature, the currents to be measured were very small, typically 10^{-9}–10^{-11} A, so the sample chamber was mounted in a Keithley Model 6104 shielded test enclosure to reduce electrical noise. Two main types of experiment were carried out in the present work. In the first, the electrical conductivity was first measured for 2 min with the sample in clean air, then for 5 cycles of 2 min in an NO_2–air mixture followed by reversal in clean air for 2 min, with concentrations of 1,

2, 3, 4 and 5 ppm in successive exposure cycles. The second type of experiment explored the reproducibility of the response to a single NO_2 concentration (3 ppm) in a similar sequence of 5 exposure and reversal cycles. Similar cycles of measurements were also made for some samples using 10–50 ppm of ammonia, or 5 successive cycles with 20 ppm ammonia.

Results and Discussion

Metal-free Crown-ether-substituted Phthalocyanines

Fig. 2–4 show the responses of the 15-crown-5, 18-crown-6 and 21-crown-7 phthalocyanine films to 1–5 ppm NO_2 and 5 cycles of 3 ppm NO_2. Repeat measurements on separately prepared films of the same materials gave results showing similar response and reversal curve shapes, although the size of the response varied by up to one order of magnitude for different films. These variations are most likely to result from differences in film thickness, which is difficult to control with the solution film deposition method used, and are consistent with some contribution arising from NO_2 diffusing into the bulk of the films. Comparison of the data for the three compounds shows that the response speed (as judged by the extent to which the conductivity increase has achieved an equilibrium value after 2 min) and the reversibility follow the order 15-crown-5 > 18-crown-6 > 21-crown-7. The response of the 15-crown-5 compound in particular is rapid and nearly completely reversible in these conditions even at room temperature. This feature is unique among the materials thus far reported in the literature, with the possible exception of lead phthalocyanine films subjected to extreme heat treatment at 360 °C.[3,4]

Electron microscope photographs of the films (Fig. 5) showed pronounced differences in morphology, with the 15-crown-5 film having a polycrystalline needle structure, the 18-
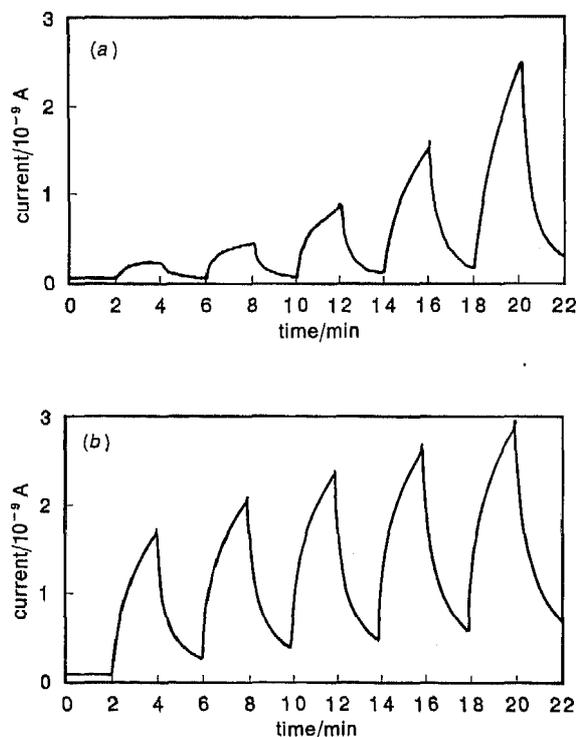
Fig. 2 Semiconductivity changes at room temperature in a film of 15-crown-5 metal-free phthalocyanine exposed to clean air for 2 min, followed by exposure to (a) 1, 2, 3, 4 and 5 ppm NO_2 in dry air for 2 min, and (b) five separate periods of 2 min of 3 ppm NO_2 in dry air, with reversal in clean air for 2 min between each exposure
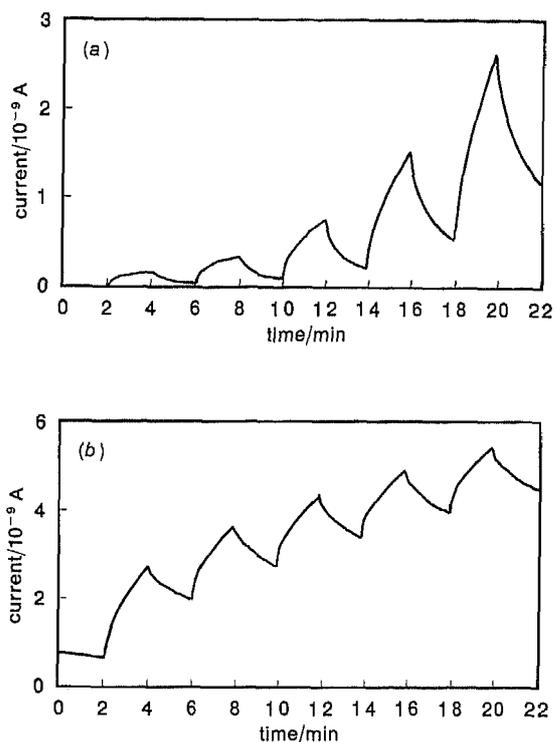
Fig. 3 Semiconductivity changes at room temperature in a film of 18-crown-6 metal-free phthalocyanine exposed to NO_2 concentration cycles as for Fig. 2
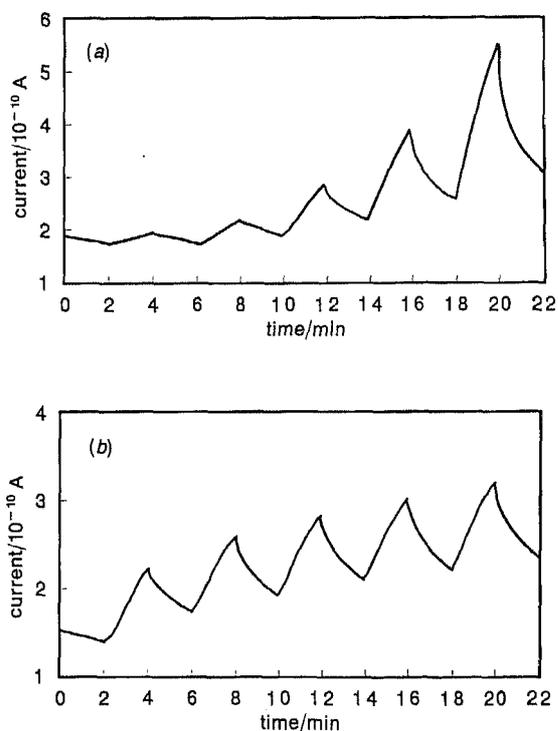

Fig. 4 Semiconductivity changes at room temperature in a film of 21-crown-7 metal-free phthalocyanine exposed to NO_2 concentration cycles as for Fig. 2

Fig. 5 SEM photographs of the films giving the data in Fig. 2–4: (a) 15-crown-5, (b) 18-crown-6, (c) 21-crown-7. (The linear structures, appearing as lighter bands in the 18-crown-6 photograph, are the electrode structures)

crown-6 film being almost completely uniform and featureless and the 21-crown-7 film apparently amorphous but cratered. Although the 15-crown-5 film morphology provides a larger surface area, which may contribute to the larger response, these differences in morphology do not account completely
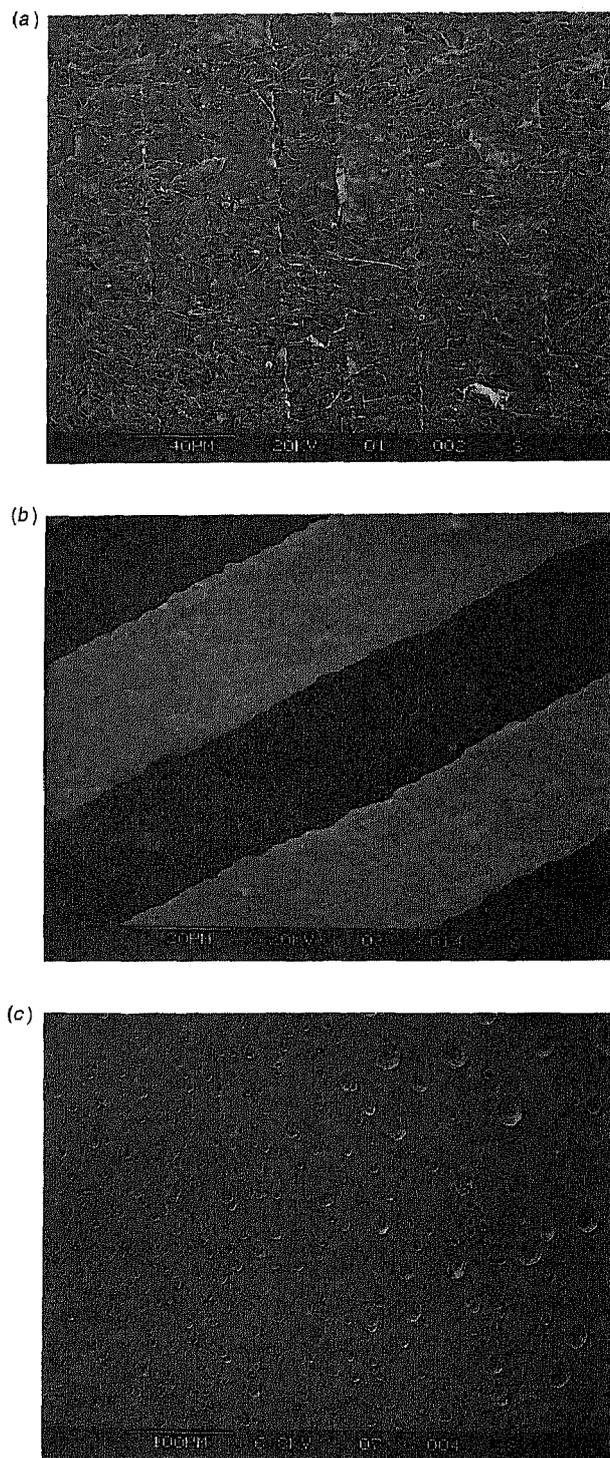
for the observed trends in NO_2 response. The differences do, however, correlate with the molecular sizes in a logical way. The four crown-ether moieties in all cases act as spacers between neighbouring molecules, with the 21-crown-7 providing the largest intermolecular lateral separation and 15-crown-5 the smallest. We have shown previously[5] that the response kinetics of phthalocyanine films in gas-sensing applications are strongly influenced by the lateral electrostatic repulsions

between negatively charged electron-acceptor molecules adsorbed on the surface. In particular, the response to gases such as NO_2 appears to be determined by the rate of displacement of adsorbed oxygen, which is accelerated by lateral repulsions with traces of strongly bound NO_2. If the lateral spacing between molecules is increased, these repulsion effects will also be reduced, leading to slower response and poorer reversibility. This model accounts for the differences between the responses shown in Fig. 2–4.

The rapid response of the 15-crown-5 compound compared with typical unsubstituted phthalocyanines at similar temperatures suggests that the surface charge-transfer interactions which lead to weak chemisorption of electron-acceptor gases on these materials are weaker for the crown-ether substituted compounds. The energy needed to transfer an electron from the phthalocyanine film to the adsorbed electron-acceptor gas molecule is determined by the ionisation potential of the phthalocyanine (which is unlikely to be strongly influenced by the crown substituents), the electron affinity of the acceptor gas and the polarisation energies of the resulting charged species. It is the latter quantities which play the most important role in the crown-ether substituted materials. The four crown-ether groups represent a considerably less polarisable environment than the π-electron systems of the phthalocyanine ring. Thus the energetics of the surface charge-transfer process are less favourable and the gases are more weakly bound, though still sufficiently strongly interacting to facilitate the charge-carrier generation process. There appears to be a delicate balance between the effects of increasing molecular size in reducing the lateral repulsions between adsorbed species (which is an unfavourable thing to do from the point of view of fast response and reversal) and reducing the polarisation energy (which has a favourable influence). This leaves considerable scope for further synthetic chemistry attaching a wider variety of spacer groups onto the phthalocyanines.

Copper Complexes of Crown-ether-substituted Phthalocyanines

Results of a broadly similar nature were obtained for the copper complexes of the 18-crown-6 and 21-crown-7 compounds, as shown in Fig. 6 and 7, although careful examination of Fig. 4 and 7 shows significant differences between the metal-free and copper complexes of the 21-crown-7 derivative. Thus, the responses to increasing NO_2 concentrations increase monotonically for the metal-free derivative, whereas for the copper complex they peak at 2 ppm and thereafter decrease. Also, for the repeated exposures to 3 ppm NO_2 for the metal-free compound the increases are similar for all five exposures, and the reversal becomes slightly better in the later cycles, whereas for the copper complex both the increases and the reversals decrease in magnitude on successive cycles. These differences can be explained in terms of the well-known tendency of copper(II) to prefer tetragonal six-fold co-ordination in a Jahn–Teller distorted environment. This enhances binding of NO_2 molecules near the centre of the large molecule, whereas for the metal-free compound the gas must adsorb on the π-electron cloud around the periphery of the phthalocyanine ring. NO_2 bound near the centre of the molecule exerts the lowest possible repulsion on neighbouring gas molecules, thus reducing the response and reversal rates as observed. The behaviour of all these materials is therefore explicable in terms of theories already developed to account for the behaviour of unsubstituted phthalocyanines. While it is encouraging that no drastically new models are required to account for the properties of these quite strongly different materials, further studies by different techniques (for example,
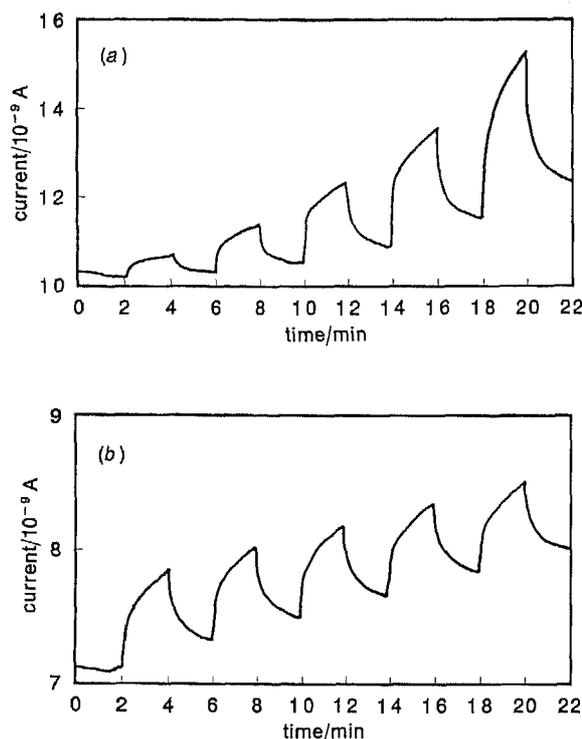

Fig. 6 Semiconductivity changes at room temperature in a film of 18-crown-6 copper phthalocyanine exposed to NO_2 concentration cycles as for Fig. 2
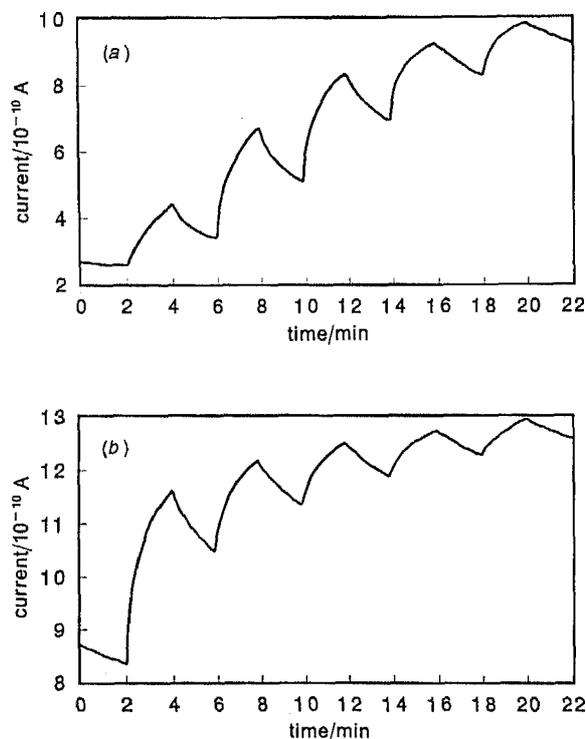

Fig. 7 Semiconductivity changes at room temperature in a film of 21-crown-7 copper phthalocyanine exposed to NO_2 concentration cycles as for Fig. 2

direct measurement of the strengths of surface interactions[6]) and on a wider range of materials with different central metal ions and different large spacer groups are needed to confirm the generality of the interpretations proposed here.
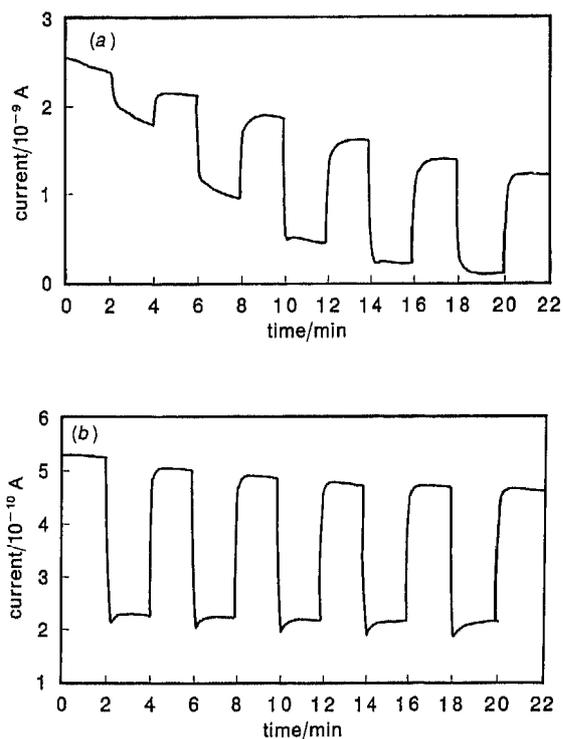
Fig. 8 Semiconductivity changes at room temperature in a film of KCl treated 15-crown-5 metal-free phthalocyanine exposed to NO$_2$ concentration cycles as for Fig. 2
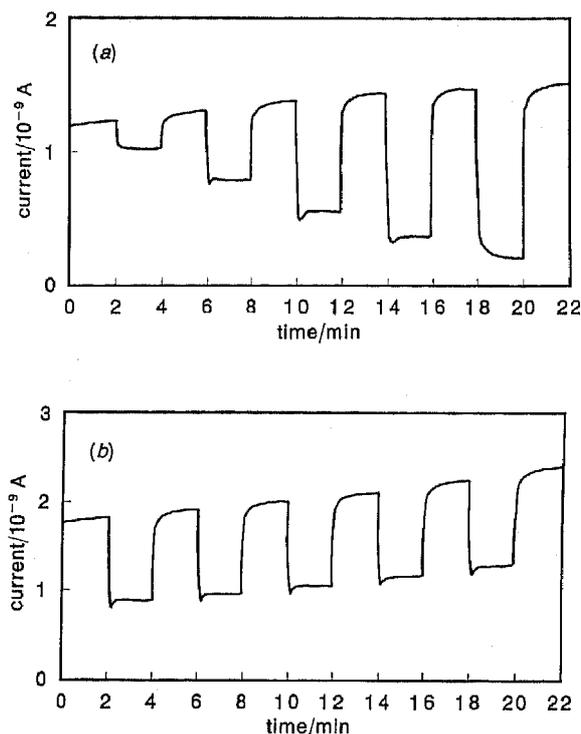

Fig. 10 Semiconductivity changes at room temperature in a film of KCl treated 21-crown-7 metal-free phthalocyanine exposed to NO$_2$ concentration cycles as for Fig. 2
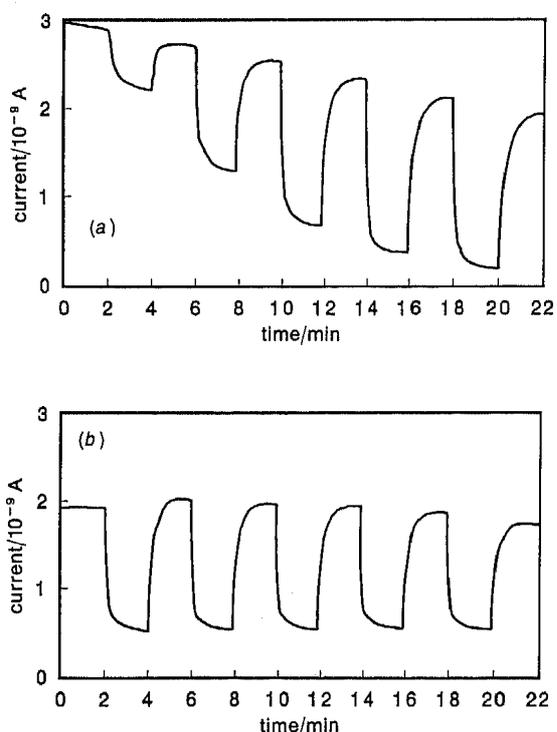

Fig. 9 Semiconductivity changes at room temperature in a film of KCl treated 18-crown-6 metal-free phthalocyanine exposed to NO$_2$ concentration cycles as for Fig. 2

Effects of KCl Treatment

Fig. 8–10 show the effects of NO$_2$ on the electrical conductivity of the same films used for the experiments of Fig. 2–4, after treatment with KCl solution. The change in response characteristics is remarkable. The initial conductivities of the

KCl treated films are *ca.* an order of magnitude larger than before treatment, and the effect of NO$_2$ is to cause an immediate rapid decrease in the conductivity. This decrease is equally rapidly and completely reversed in clean air. Fig. 11 shows the scanning electron microscope images of the surfaces of the KCl treated 15-crown-5 and 18-crown-6 films. The surface structure of the 15-crown-5 film has become dramatically more uniform, with complete loss of the needle crystallite morphology, while the 18-crown-6 film shows signs of a slightly rougher texture than before treatment, which on higher magnification is seen to be a consequence of the deposition of small crystallites onto the film surface. It seems likely that these crystallites are of KCl, but further work is needed to prove this and to show whether or not the effects on electrical properties can be obtained without the deposition of such crystallites if the KCl treatment is optimised. These results suggest that the KCl treatment increases the n-type contribution to the film conductivity, which is then reduced by depletive chemisorption of NO$_2$.

Alkali-metal salts are well known to complex with crown ethers, and the effect is related to the relative sizes of the alkali-metal ion and the central cavity in the crown ether.[7] The cavity radii (determined from CPK models[8]) are 0.86–0.92 Å for 15-crown-5, 1.34–1.43 Å for 18-crown-6 and 1.7–2.1 Å for 21-crown-7, while the potassium ion radius is 1.38 Å. Thus the ion will fit into the 18-crown-6 and 21-crown-7 cavities, but not into the 15-crown-5 cavity. The effects of alkali-metal salts on the molecular assembly of crowned phthalocyanines have been discussed,[2] and cations which are too large to fit into the cavities serve to bridge crown-ether moieties of two different phthalocyanine molecules and thus promote structural ordering. In the case of cations which will fit into the cavities, it is believed that the counter-anions strongly prefer locations close to the cations on electrostatic grounds, and therefore intercalate between adjacent crowned phthalocyanine molecules containing up to four potassium
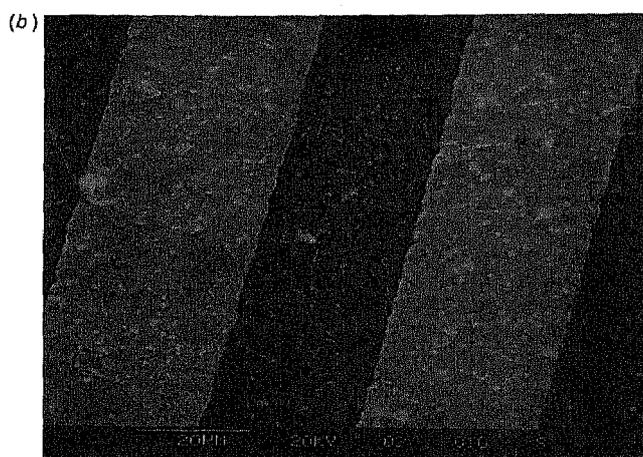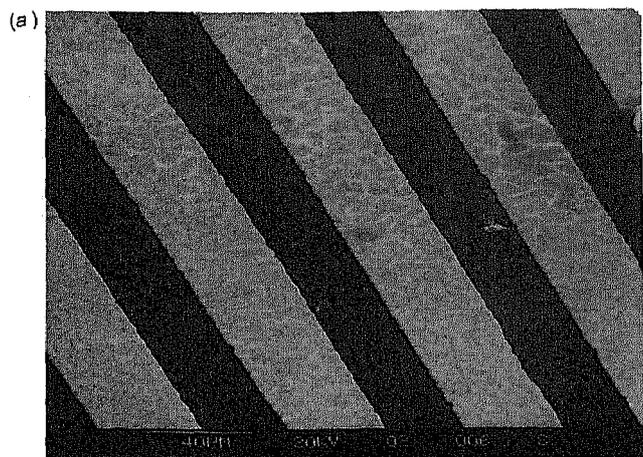
Fig. 11 SEM photographs of KCl treated films: (a) 15-crown-5, (b) and (c) 18-crown-6

Fig. 12 Calibration curves in 1–5 ppm NO_2 for KCl treated metal-free phthalocyanine sensors at room temperature: (a) 15-crown-5, (b) 18-crown-6 and (c) 21-crown-7

ions each, forming equally strongly ordered structures. These tight structures are in marked contrast to the relatively porous structures of the parent crowned phthalocyanines, and may severely limit the ingress of oxygen into the films. This may be the origin of the loss of p-type conductivity in the films. Although it might be expected that this effect would lead to a lower initial conductivity in the films, the tighter structure will also greatly enhance the electron transport properties of the material, and this would account for the observed higher conductivity in clean air. Furthermore, the improvement in
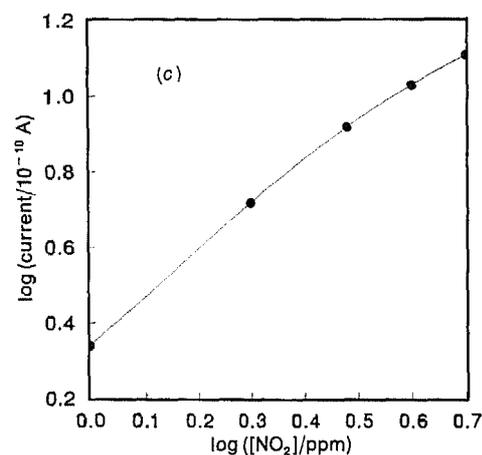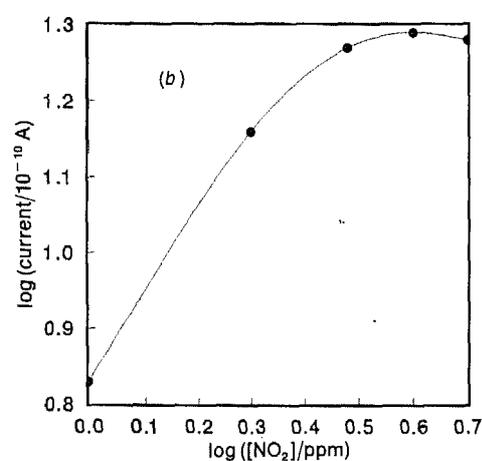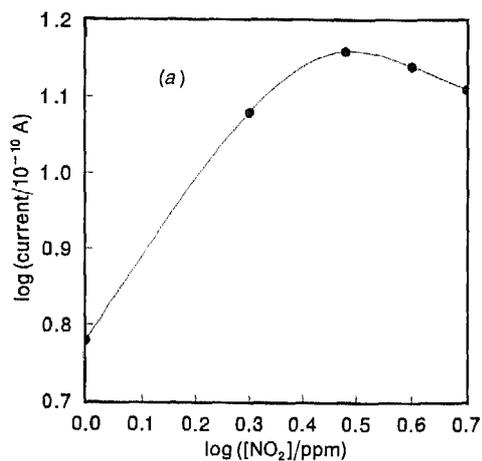
surface uniformity of the film would minimise the number of strong adsorption sites, grain boundaries and pathways for slow diffusion of gases into the bulk of the film, which are all contributors to slow components in the response of the semiconductivity to adsorbed gases.

A mechanism involving depletive chemisorption also predicts that in the presence of higher concentrations of NO_2 the observed decrease in conductivity should become smaller and eventually change sign as p-type doping dominates. Fig. 12 shows calibration curves for the KCl treated sensors,
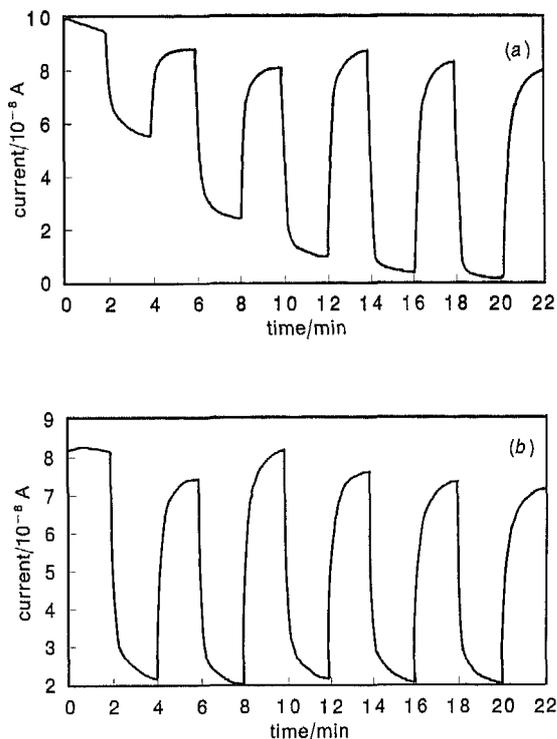
Fig. 13 Semiconductivity changes at room temperature in a film of KCl treated 15-crown-5 metal-free phthalocyanine exposed to clean air for 2 min, followed by exposures to (*a*) 10, 20, 30, 40 and 50 ppm NH_3 in dry air for 2 min, and (*b*) five separate 2 min periods of 20 ppm NH_3 in dry air, with reversal in clean air for 2 min between each exposure

from which it is clear that the response of the 15-crown-5 compound is already showing clear signs of such a reversal above NO_2 concentrations of *ca.* 3 ppm, while the trend is progressively weaker for the other two compounds. It is not yet known whether this trend is associated with differences

in molecular assembly or differences in impurity content for the different materials.

As a test of the proposed depletive chemisorption mechanism for the above effects, experiments were carried out for a fresh film of the 15-crown-5 compound treated with KCl and then exposed to ammonia in various concentrations. As shown in Fig. 13, ammonia (a donor gas) also produces a negative response, suggesting depletive chemisorption on a p-type material. The result suggests that the KCl treated films may have both donor and acceptor impurity levels contributing to the conductivity, so that both acceptor and donor gases can lead to depletive chemisorption. As this was a fresh film, no comparison can be made of the magnitudes of the effects of NO_2 and NH_3.

The results described herein prove that crown-ether phthalocyanines proffer a rich and varied research field. In particular, the dramatic results obtained for the materials reported here clearly demonstrate their potential for gas-sensing devices, because the rapidity and reversibility of the effects are superior to those of other materials of the phthalocyanine class so far proposed for gas-sensor applications.

References

1 J. D. Wright, *Prog. Surf. Sci.*, 1989, **31**, 1.
2 O. E. Sielcken, M. M. van Tilborg, M. F. M. Roks, R. Hendriks, W. Drenth and R. J. M. Nolte, *J. Amer. Chem. Soc.*, 1987, **109**, 4261.
3 T. A. Jones, B. Bott and S. C. Thorpe, *Sensors and Actuators*, 1989, **17**, 467.
4 Y. Sadaoka, T. A. Jones and W. Göpel, *Sensors and Actuators*, 1990, **B1**, 148.
5 P. B. M. Archer, A. V. Chadwick, J. J. Miasik, M. Tamizi and J. D. Wright, *Sensors and Actuators*, 1989, **16**, 379.
6 R. C. Weaver and J. D. Wright, *Sensors and Actuators*, 1991, **B4**, 505.
7 P. D. Beer, in *Chemical Sensors*, ed. T. E. Edmonds, Blackie, London, 1988, p. 22.
8 N. K. Dalley, in *Synthetic Multidentate Macrocyclic Compounds*, ed. R. M. Izatt and J. J. Christensen, Academic Press, New York, 1978, p. 207.