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Effects of metal salts on structural, electrical and gas-sensing properties of crown-ether-substituted phthalocyanines and related compounds

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Abstract

The effects of nitrogen dioxide on the semiconductivity of crown-ether-substituted phthalocyanines and related aza-crown phthalocyanines in both dry and humid conditions are reported, for films deposited from chloroform solution and doped with different metal salts. Humidity changes the response to NO₂ from a p-type conductivity increase to an n-type decrease. Replacing one oxygen atom in each crown ring by N-acetyl blocks the crown cavity and minimises effects of water and added salts. Replacing more oxygens with N-tosyl groups leads to strong steric effects and very poor conductivity in all environments. The effects of doping with other metal salts are also discussed.

Introduction

Recently we described the dramatic improvements in phthalocyanine NO₂ sensors which we obtained at room temperature by using films of phthalocyanines functionalised by four crown-ether rings (Fig. 1) [1]. Films deposited from chloroform solution showed response rates and reversibility at room temperature which were superior to those of previously studied phthalocyanine derivatives. These characteristics can be explained in terms of the low polarisability of the local environment of the phthalocyanine cores, which reduces the polarisation energy associated with charged species in the crystal. This weakens charge transfer interactions between adsorbed electron acceptor gases and the surface of the film, giving more rapid displacement of surface oxygen species by NO₂ as well as more facile desorption of NO₂ on exposure to clean air. Increasing the size of the crown-ether rings was found to produce slower, less reversible effects due to the reduction in lateral repulsions between adsorbed species. We have previously discussed the importance of these repulsions in determining the response kinetics of this class of gas sensors [2]. Doping these films with potassium chloride led to extremely rapid conductivity decreases on exposure to NO₂ which reversed equally rapidly in clean air. This was unexpected, but was

interpreted in terms of improved molecular assembly induced by complexing of the metal ions with the crown-ether groups [1]. In this paper we explore these phenomena in more detail, using varying humidity, modified crown-ether groups, and different metal salts.

Effects of humidity

The KCl doped films were prepared by treatment of the undoped films with one drop of a 1 g/l aqueous solution of potassium chloride followed by drying by natural evaporation of the water at room temperature in a dust-protected chamber; the previous measurements [1] were all made in a constant flow of 600 ml/min of dry air or (dry air + NO₂) immediately after the film surface appeared dry. A further series of experiments using a different test rig in which the dry air flow varied up to 7 l/min, with the films allowed to dry overnight in the air flow, consistently yielded different results in which the current *increased* on exposure to NO₂. After extensive equipment checks to ensure that the observed effects were not due to temperature variations or different NO₂ concentration ranges, these differences were traced to different humidity effects on the films. Figure 2 shows the response of a KCl-doped film of the 18-crown-6 metal-free phthalocyanine to a 2

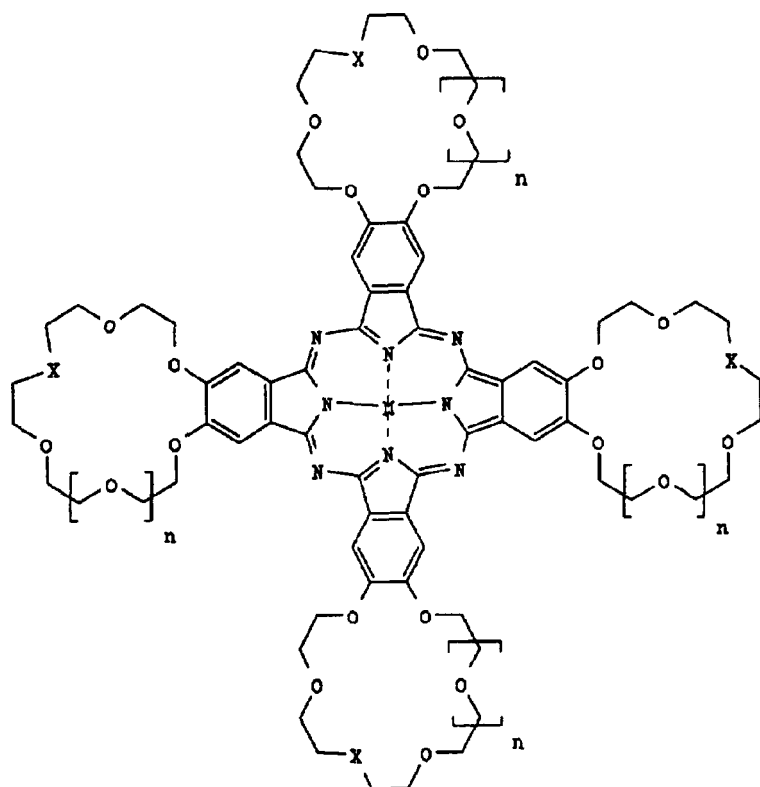


Fig. 1. $M = 2H$ or Cu ; $n = 0, 1$ or 2 ; $X = O$ or $N-COCH_3$.

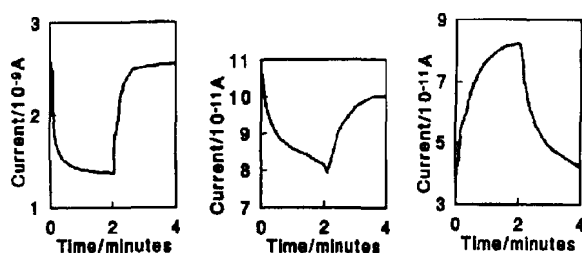


Fig. 2. Response of the semiconductivity of a KCl-doped 18-crown-6 metal-free phthalocyanine film to a 2 min exposure to 1 ppm of NO_2 in dry air followed by reversal in clean dry air for 2 min: (a) immediately after initial drying of the excess water, (b) 1 h later, (c) 20 h later.

min pulse of 1 ppm of NO_2 in dry air followed by a 2 min reversal in clean dry air, immediately after mounting in the rig and at intervals of approximately 1 and 20 h later. A gradual transition from the decrease in conductivity on exposure to NO_2 (n-type behaviour) to an increase in conductivity can be seen. This suggests that the film behaves as a p-type semiconductor in dry conditions but as a rather better n-type conductor in humid conditions, and that possibly some of the effects earlier attributed to the onset of depletion of the n-type conduction and return to dominance of p-type conduction may have in fact been due to drying out of the film. To explore these effects further, experiments were

carried out with the higher flow rates of up to 7 l/min, first in dry air after allowing the film to equilibrate overnight in the dry conditions, then with the relative humidity of both the clean and NO_2 -containing air controlled to 33% using bubblers with saturated magnesium chloride solution before the air passed over the NO_2 permeation vial, and finally in dry conditions once again after adequate equilibration. Figure 3 shows the results of these experiments for a film of the 15-crown-5 metal-free phthalocyanine after treatment with KCl solution, confirming that the p-type response in dry air changes to an n-type response in humid air, and finally back to a p-type response on further exposure to dry conditions.

The oxygen atoms of the crown-ether groups, together with the nitrogen atoms of the phthalocyanine core, provide many sites for hydrogen bonding of water molecules. Water molecules in the films may have several effects: (i) they may mobilise any uncomplexed added salt, leading to improved film structuring and a possible contribution from ionic conductivity; (ii) they may occupy voids in the film structure, preventing ingress of oxygen or NO_2 ; (iii) they may influence the structure of the film by forming hydrogen-bonded bridges between crown rings of different molecules. The combined influence of these effects will be to produce an ordered film (with correspondingly high charge carrier mobility and hence higher conductivity). Oxygen is

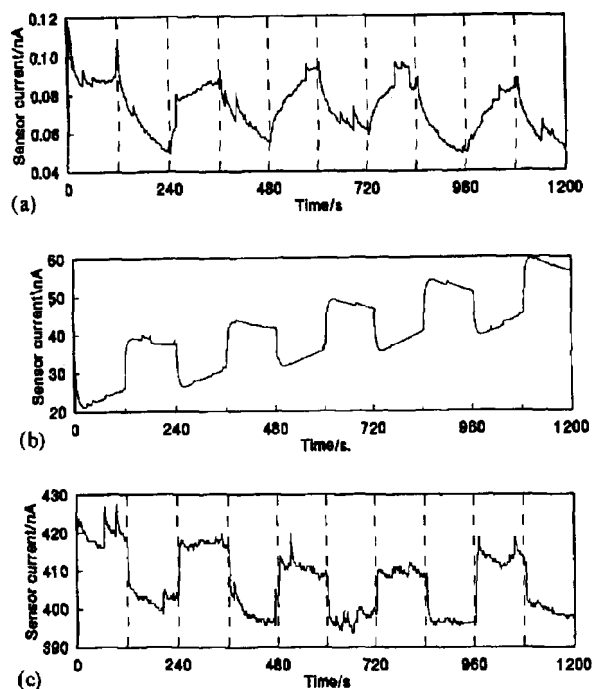


Fig. 3. Response of the semiconductivity of a KCl-doped 15-crown-5 metal-free phthalocyanine film to 5 cycles of exposure for 2 min to 1 ppm of NO_2 with reversal for 2 min in clean air: (a) after drying the film at room temperature overnight, (b) in 33% relative humidity, (c) in dry conditions after further drying to equilibrium.

then confined to the surface of the film and the only charge carriers in clean air conditions are those produced thermally from the material itself rather than as a consequence of charge-transfer processes with oxygen. From the observed decrease in conductivity on exposure to NO_2 it is clear that this background conductivity is n-type. As the film dries out, voids are re-exposed and the hydrogen-bonded bridges between molecules are degraded producing a film which is less structured, reducing charge carrier mobility. Thus, even though oxygen can now diffuse into the bulk giving a p-type conductivity, the overall conductivity is poorer than in the presence of water. The response to strong electron acceptors such as NO_2 is now a conductivity increase, confirming the background dominant p-type conductivity due to the presence of oxygen. The results shown in Fig. 3 demonstrate that these initial drying-out effects are reversible in humid air, and that subsequent re-drying gives a conductivity of the order of $10^4 \times$ that of the original doped material after the first drying although the conductivity increase on exposure to the same NO_2 concentration is only $500 \times$ greater than for the original material. This is consistent with a well-structured film, possibly containing some residual oxygen trapped between bulk water molecules, whose surface area accessible to electroactive NO_2 molecules is lower than that of the original film.

The change in the sign of the NO_2 response in humid conditions provides a clear warning that humidity is influencing the measured response. In contrast, the response of unsubstituted phthalocyanines decreases substantially in humid conditions and there is no indication from the sensor output whether this effect is due to humidity or to a genuine reduction in ambient NO_2 concentration. Calibrations over wider concentration and humidity ranges are in progress.

Studies with related substituted phthalocyanines

In view of the above discussion, it is particularly interesting to explore the effect of blocking the cavities in the crown-ether rings by appropriate substituents. This should show whether metal salts which are not strongly complexed by the crown rings have any effect on the conductivity and gas-sensing properties. It should also show how far the effects of water can be minimised when hydrogen bonding with the crown oxygens is sterically hindered. For this purpose we have used an aza-15-crown-5 copper phthalocyanine analogous to the 15-crown-5 parent but with the outermost oxygen in each crown ring replaced by N-acetyl (Fig. 1; $M = \text{Cu}$, $n = 0$, $X = \text{N-COCH}_3$). Although models show that the acetyl group does not completely fill the central cavity and some interaction with alkali metal ions is still possible [3], it is large enough to prevent most metal ions from entering right into the cavity. Thus it will clearly disrupt the structure-enhancing effects of interactions between the crown ligand atoms and either metal ions or water molecules. This is clearly shown in scanning electron microscope images of the film surface before and after treatment with KCl, which are virtually identical, in marked contrast to the dramatic improvement in surface smoothness observed [1] when the films of 15-crown-5 metal-free phthalocyanine were treated with KCl. Figure 4 shows the conductivity changes in cycles of 2 min exposure to 1, 2, 3, 4 and 5 ppm NO_2 with exposure to clean air between each exposure, for films of this compound both before and after treatment with KCl solution, and in both dry air and air of approximately 10% relative humidity. The responses for KCl-doped and non-doped films are very similar, with the minor differences in conductivity possibly arising from changes in film thickness. This proves that metal ions which are not strongly interacting with the crown ligand atoms have very little influence on properties of the film. In humid air the conductivities of both doped and undoped films are increased but the gas effects still remain p-type, with conductivity increasing. This suggests that water is still able to improve the film structure but not to the same extent as in the case of the parent crowns which contain only oxygen ligand atoms.

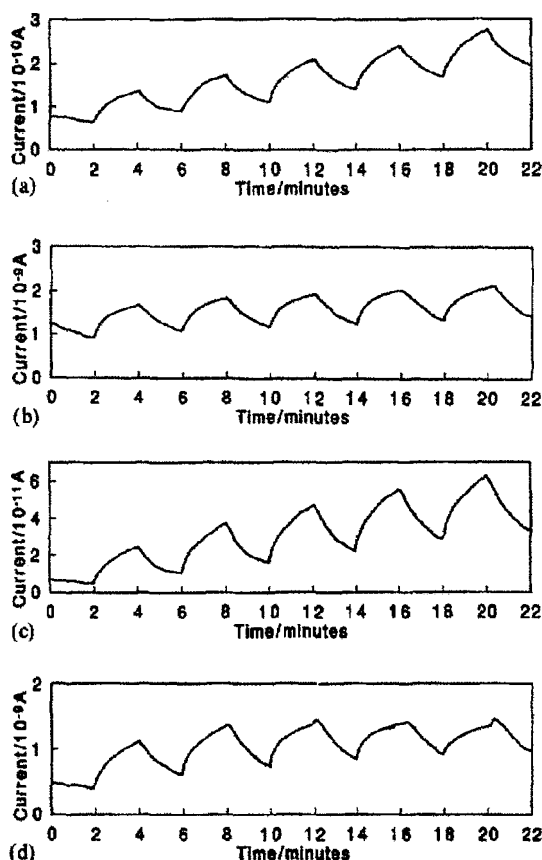


Fig. 4. Response of the semiconductivity of films of the azacrown copper phthalocyanine (Fig. 1, $M = \text{Cu}$, $n = 0$, $X = \text{N-COCH}_3$) to clean air for 2 min then to 1, 2, 3, 4 and 5 ppm NO_2 in air for 2 min periods with reversal in clean air for 2 min after each exposure: (a) in dry conditions before doping, (b) in approximately 10% relative humidity before doping, (c) in dry conditions after KCl doping, (d) in approximately 10% relative humidity after KCl doping.

Interestingly, this conductivity increase in KCl-treated films is no greater than in untreated films. This eliminates the possibility of significant ionic conductivity contributions, which should become larger when the films contain more water. All of these experiments show slower response and reversal characteristics than for the parent 15-crown-5 metal-free compound. This is in part due to the higher polarisability of the nitrogen atom, which increases the strength of charge-transfer interactions, but also due to the presence of the central copper atom which draws adsorbed NO_2 towards the centre of the molecule, thus reducing the lateral repulsions between adsorbed species which facilitate rapid adsorption and desorption [2].

Similar experiments with a copper phthalocyanine substituted with four tetra-tosylated tetraazacyclopentadecine rings showed that this material was an extremely poor conductor whose films gave currents in the order of 10^{-14} A in all conditions. The strong steric

hindrance from the four toluene sulfonate groups which are forced to lie out of the main plane of the molecule presumably reduces intermolecular overlap to such an extent that no conduction pathway is available.

Effects of doping with different metal ions

The experiments reported in ref. 1 have been extended to doping with RbCl. Figure 5 shows the response of the RbCl-doped films to the same cycle of exposures as that for Fig. 3. The initial response to NO_2 in dry air is significantly larger and less reversible than for the KCl-doped film, and responses on successive exposures to the same NO_2 concentration increase in magnitude. In contrast, both the n-type response in humid conditions and the recovered p-type response on re-drying are much smaller than for the KCl-doped samples. This suggests that the larger Rb^+ ion (Pauling ionic radius 1.48 Å; cf. K^+ , 1.33 Å) is less effective at promoting molecular assembly by interaction with the small 15-crown-5 rings (cavity radius 0.86–0.92 Å), and that the carrier mobility is limited by the larger inter-ring distance enforced by the large Rb^+ ion bridging crown rings of two adjacent phthalocyanines. Preliminary results have been obtained for films doped with other metal salts. However the complications introduced by possible variations in extent of complexing,

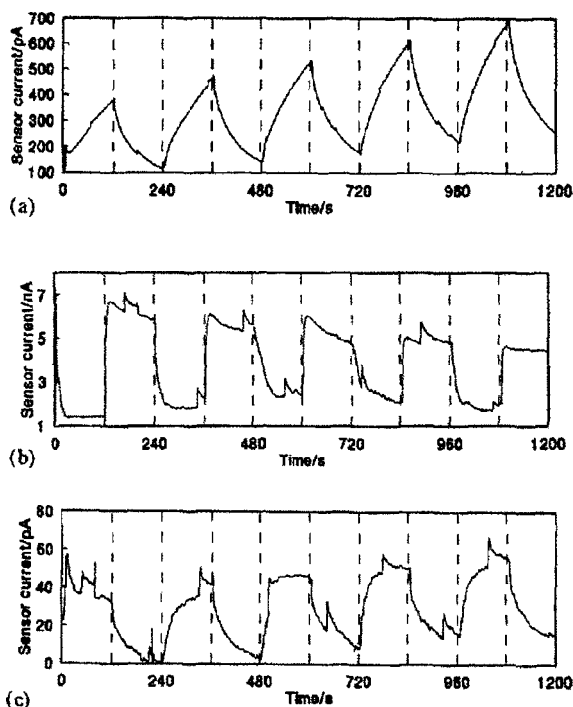


Fig. 5. Response of an RbCl-doped film of 15-crown-5 metal-free phthalocyanine to the same sequence of exposures as used in Fig. 3.

hygroscopic character of the salts and quality of film deposition from solution mean that further experiments are needed before secure conclusions can be drawn. Spin-coating has recently been shown to be a promising way of improving the reproducibility of film deposition for these materials [4].

Conclusions

This work shows that the NO₂-sensing properties of the crowned phthalocyanine films doped with metal salts are more complex than originally suggested. However, the sensor performance of these materials remains superior to that of previously reported phthalocyanine films, with faster response and reversal at room temperature combined with distinctive changes in type of response providing warning of humidity effects. There is considerable scope for further performance improvements by chemical variation and improved film deposition methods.

Acknowledgements

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