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Sterically hindered phthalocyanines: solid-phase interactions with carbon monoxide in matrix-entrapped thin functional films

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Abstract A thin film comprising highly sterically hindered iron phthalocyanine derivatives incorporated into sol–gel networks shows effective sensitivity to carbon monoxide gas, when monitored by UV–visible absorption spectroscopy at 670 nm. The absorbance of a sol–gel thin film incorporating octaphenyl-di-tert-butylphthalocyanine iron(II) was particularly sensitive to carbon monoxide gas and showed a change in absorption after exposure to 1000 ppm CO gas for 1 min, while repetitive exposures produced only a limited loss of response. The optical response of the thin film gradually decreases with increasing temperature, and the binding energy for this sensing phenomenon was calculated to be 0.401 eV. The spectrum recovers at room temperature some 5 min after exposure to the gas.

Introduction

Sensing for gases in the ambient environment is an important research objective, and any new sensor system should be chemically selective, reversible, fast, highly sensitive, durable and insensitive to contamination or ‘poisoning’. It ought to be simple in operation, of a small size, simple to fabricate, relatively insensitive to temperature, with low noise, and low manufacturing costs [1].

An important gas for sensing, because of its prevalence in the ambient environment, especially in the home, is the toxic gas carbon monoxide. There are a number of different electronic, electrochemical and redox sensor systems employed for this target, each offers different benefits for effective commercialisation, and suffers from different drawbacks [2–5]. Optical sensors are highly demanded as they can be used for chemical and biological molecules [6]. This report concerns an optical sensing methodology for CO sensing. The toxicity of this gas is due to its interaction with the iron porphyrin unit of haemoglobin, which is accompanied by a change in visible absorption spectroscopy. However, it has yet to prove practical to use this phenomenon for a commercial sensor, due to poor solubility and intractability of the phthalocyanine, and in particular the prevalence of aggregation effects, in which the disc-like complexes stack together so as to limit access of target gas to molecules at the centre of the assembly, which diminishes the spectroscopic changes that are observed. Iron(II) phthalocyanine sensitivity to gases such as CO and NO_2 has been improved by solubilised phthalocyanine with N-donor ligand and incorporated into nanoparticulate metal oxide matrix, optical sensor could be develop as N-donor ligand permit ligand exchange with gas molecule easily [7]. Our aim in this work is to minimise these negative solubility and aggregation phenomena, and to enhance sensitivity of the gas interaction process by modifying the electron-density on the macrocyclic ring [8]. To this end we earlier reported the synthesis of highly sterically hindered iron(II) phthalocyanine derivatives, and their response to carbon monoxide in solution phase studies [8]. However, for a practical commercial sensor solid-phase operation is desirable, and we now report the entrapment of substituted iron phthalocyanine derivatives in thin solid film matrices and the consequences monitored by absorption spectroscopy upon their exposure to carbon monoxide gas. The advantage of such a thin film system operating by optical change is that in principle a straightforward and

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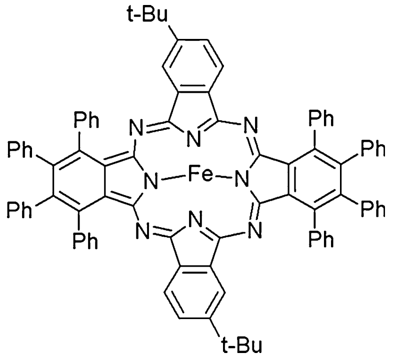

Structure 1 Octaphenyl-di-tert-butylphthalocyanine iron(II)

economic sensor may be fabricated, using for example an LED light source, a simple photodetector, and using a minimal amount of functionalised active component matrix-entrapped in a low geometric area of the key sensor element.

The bulky substituents chosen for this work were a mixture of phenyl rings and *t*-butyl groups, with the main compound studied octaphenyl-di-tert-butylphthalocyanine iron(II) (Structure 1) (it is not possible to make quantities of all-phenyl-substituted hexadecylphenylphthalocyanines due to excessive steric hindrance).

Experimental

Materials

The following were purchased from Aldrich and used without further purification: iron phthalocyanine, *N*,*N*-dimethylformamide 99%, dimethylsulfoxide 99%, carbon monoxide 99%, triton x-100, tetraethyl orthosilicate.

The procedure for synthesis of the functionalised phthalocyanine iron(II) derivative has been reported elsewhere [8]. In summary it is synthesised from a mixture of tetraphenylphthalonitrile and *t*-butyl phthalonitrile starting materials heated with an iron salt, and the desired isomer separated from the major impurity tetra-*t*-butyl phthalocyanine and minor isomeric product impurities by column chromatography.

Instrumentation: Perkin Elmer Lamda 25 UV/Vis spectrometer, Fire Angel CO sensor.

Sol–gel process

Sol–gel films were prepared by the acid catalyzed hydrolysis and condensation of silicone alkoxide precursors. Several trials were performed using various components in different ratios in order to find the best ratio for effective thin film formation. This general procedure was used for all trials:

A mixture of tetraethyl orthosilicate (TEOS), absolute ethanol, and Triton x-100 were mixed together for 1 h. Octaphenyl-di-tert-butylphthalocyanine iron(II) was dissolved in either DMF or DMSO and was added to the mixture and stirred for another 45 min. The mixture was sonicated in an ultrasonic bath for 5 min, and stirred again for 10 min. Five drops of concentrated hydrochloric acid were added to the mixture, which was stirred for 30 min. Substrates were prepared using micro pipettes of 50 µL volume for spreading onto a clean glass slide. When coated with thin films these substrates were left to dry in the ambient atmosphere for 2 days (Table 1).

Exposure of thin films to carbon monoxide

Gas sensing procedure

A closed fume bag (Atombag) supplied by Aldrich was placed in a fume cupboard. A UV/Vis spectrometer was fitted inside the bag together with a carbon monoxide sensor obtained from Fire Angel®. Carbon monoxide gas was passed into the bag in various concentrations (100–1500 ppm) measured by using Fire angel sensor, and absorbance changes were measured over the range 210–900 nm. Phthalocyanine was the only component in the system to absorb towards and in the visible region. The gas sensing properties were studied at constant concentration of carbon monoxide 1000 ppm, and different temperatures 293, 298, 303, 308, and 313 K over periods of time (1–60 min), using the internal heater inside the UV equipment. Five measurements were recorded at each temperature.

Table 1 Component ratios employed in the sol–gel thin films

Trial no.	TEOS (µL)	ETOH (µL)	Triton (µL)	Pc-Fe(II) (mg)	DMF (µL)	DMSO (µL)	HCl
1	250	2100	200	5	–	300	5 drops
2	250	2000	200	5	300	–	5 drops
3	250	2000	300	1.5	300	–	5 drops
4	250	2000	300	1.5	200	–	5 drops
5	200	1500	300	2.4	300	–	5 drops

Result and discussion

Matrix entrapment

Entrapping organic molecules into thin film gives advantages for this type of gas sensor and in this work the functionalised iron(II) phthalocyanine derivatives were first entrapped in different kinds of matrix media. These included polyacrylate glues and other vinyl polymer systems, and two-part cured polysiloxane elastomers such as Dow Corning 148 [9–11]. We found that the acrylate glues and other vinyl polymers gave films prone to phase separation, so that the entrapped functional phthalocyanine derivative was not uniformly distributed, and these were not investigated further.

The two-part silicone elastomer systems suffered from a different problem. We have earlier used these most effectively for an optical gas sensor for nitrogen dioxide, in which activated azo-compounds were entrapped by mixing them in toluene solution into the two-part elastomer. This cures by a platinum-catalysed insertion reaction of a pendant R-CH=CH_2 unit in one component of the two-part cure into available Si–H bonds in the other component, giving R-CH_2CH_2-Si crosslink after curing. Toluene is driven off during drying to give tough uniform thin films of the azo-compounds entrapped in a polysilicone matrix. These gave effective responses to nitrogen dioxide, and were employed in a prototype optical sensing device of the type sought in this present work [12]. We also employed sol–gel formation of siloxane matrices to entrap azo-derivatives and found them to be equally effective.

However, when we tried to entrap the functionalised phthalocyanine derivatives in the two-part cured siloxane elastomer systems, we found that the curing reaction was inhibited, yielding at best poor-quality films, and often yielding liquids that seemed not to have cured at all. Variations of the components in the cure system could mitigate against this problem to a degree, but required systems that contained so much catalyst that upon exposure of the resultant films to carbon monoxide gas any significant result could have been art factual.

However, the use of TEOS in a typical sol–gel process produced the best thin films, with good cohesion, fine uniformity of colour and no apparent disadvantageous phase separation. These gave clear and evident optical responses in sensing tests and are the subject of the remainder of this report.

Sol–gel films

These may be prepared with different characters [11], since in this technique there are several parameters to be changed to alter properties of the resulting thin films [13]. Changes in pH can affect film porosity, a crucial parameter for gas diffusion, while using surfactant chemical species such as Tritons can help to increase the homogeneity in the mixture and increase the porosity of the resulted films [14]. The use of DMF or DMSO as co-solvents allows this technique advantages over others, since phthalocyanines have good solubilities in these solvents [15, 16], and we have earlier shown these solvents to be very effective ones for solution-phase interactions of carbon monoxide with substituted phthalocyanines [8].

When octaphenyl-di-tert-butylphthalocyanine iron(II) we entrapped in thin film with ratio of TEOS:Ethanol:Triton: Pc-Fe derivative:DMF:HCl (225 µL:1500 µL:300 µL:2.4 mg:300 µL:5 drops) a substantial response (10 min) with good recovery time (5 min) at room conditions, was observed. In addition, subsequent tests indicated that re-exposure of the film to CO continued to show significant absorbance changes and repeatability. Table 2 shows the change in absorbance, and the spectrum could be seen in Figs. 1 and 2.

To show true sensing capabilities for the thin film, a multi-step on/off cycle was applied. Figure 3 shows the response of the film when the gas switch between on/off; with this experiment the work was done in closed system,

Table 2 Two exposures to CO (1000 ppm) for compound B in sol–gel

Same slide					
First exposure			Subsequent exposure		
Time (min)	Absorbance	Sensitivity (%)	Time (min)	Absorbance change	Sensitivity (%)
0	0.2929	0	0	0.3073	0
1	0.3290	12.4	1	0.3356	9.2
5	0.3506	19.7	5	0.3601	17.2
10	0.3954	35.0	10	0.3961	28.9
20	0.4489	53.3	20	0.4513	46.8
30	0.4654	58.9	30	0.4647	51.2
45	0.4887	66.9	45	0.4983	62.1

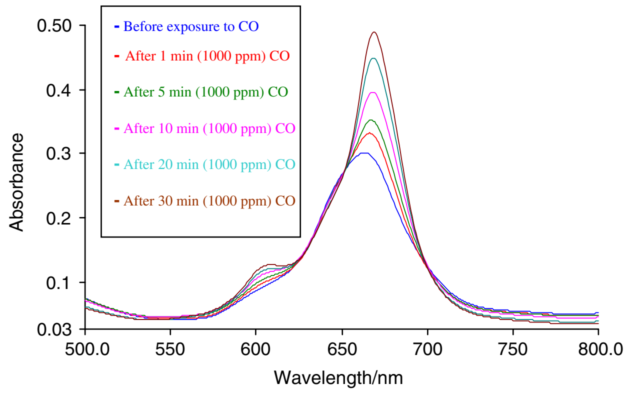

Fig. 1 Change in absorbance of octaphenyl-di-tert-butylphthalocyanine iron(II) entrapped in sol-gel thin film during exposure to CO 1000 ppm with time

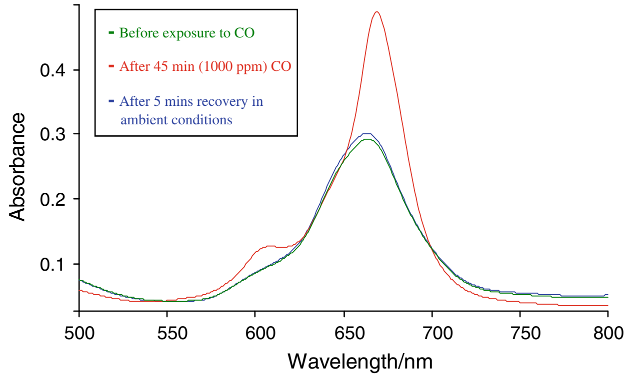

Fig. 2 Recovery for octaphenyl-di-tert-butylphthalocyanine iron(II) thin film after exposure to CO 1000 ppm

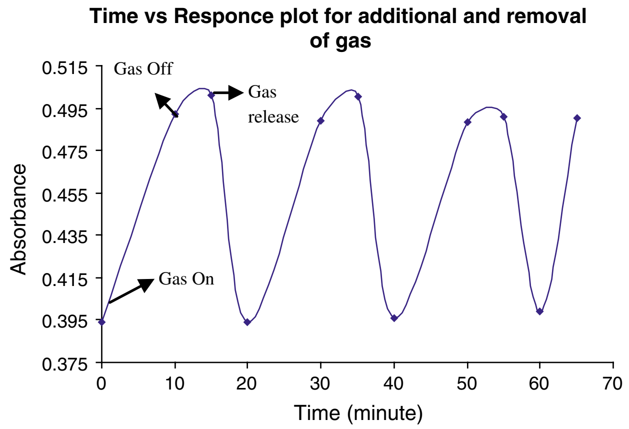

Fig. 3 Time versus response plot for additional and removal of CO gas

so the gas switch on for 10 min to have a substantial response then the gas was released from the system (which take around 5 min). However; the sensor did not reach the saturated point, and these trials have been done to check the ability of the thin film to recover and respond again after re-expose to the gas. For maximum response, see the experiment for binding energy calculation.

Binding energy using Langmuir model

In a gas sensor there is interaction between the target gas molecule and an 'active site' in the sensor, which here is in the solid state [17]. If this process is considered from an energetic viewpoint to be one of adsorption (i.e. disregarding any chemistry that might prevail), then there are several models that can describe the kinetic processes in sensors [18]. The Langmuir Adsorption Model has been widely used in the literature to describe adsorption behaviour in sensor systems, including those employing phthalocyanines and porphyrins as active sensing compounds [19, 20]. It is based on the fundamental adsorption equation:

$$n_a = I\tau_a = \left[\frac{p}{(2\pi mkT)^{1/2}}\right]\tau_0 \exp\left(\frac{\Delta H_{des}}{kT}\right)$$

where n_a is the surface population of adsorbed molecules, cm^{-2} (number of sites filled), I is the impingement rate of gas molecules to a given area of substrate, m is the mass of a gas molecule, p is gas pressure, T is temperature and k is Boltzmann constant.

The Langmuir model has several primary assumptions; homogeneity of the solid surface, independence of the energy of adsorption on the presence of other molecules, it is assumed that ΔH_{des} is the same for all sites, atoms striking a surface site that is already occupied do not adsorb. So τ_a has a finite value for atoms striking unoccupied sites, and zero value for atoms striking occupied sites [18]. In order to apply the fundamental gas equation to this model, the impingement rate must be multiplied by the factor $[1 - (n_a/n_0)]$ where n_0 is the number of absorption sites per cm^2 [18, 20]. This factor is used to allow for the fact that atoms striking occupied sites are not adsorbed. The following equation is the Langmuir adsorption equation, where at low pressures and moderate temperature a good approximation of θ can be

$$\theta \approx \left(\frac{\tau_0}{n_0}\right)\left[\frac{p}{(2\pi mkT)^{1/2}}\right]\exp\left(\frac{\Delta H_{des}}{kT}\right)$$

where τ_a is mean surface lifetime of gas molecules at the adsorbent, τ_0 is the standard mean surface lifetime of gas molecules at the adsorbent, n_a is the surface population of adsorbed molecules, cm^{-2} (number of sites filled), n_0 is the number of absorption sites per cm^2, m is the mass of a gas molecule, p is gas pressure, T is temperature, k is

Boltzmann constant, and ΔH_{des} is adsorption activation energy [18, 20].

Assuming that the change in fractional surface coverage is proportional to the change in absorbance (ΔAbs) as a function of temperature, so the final equation

$$\ln \Delta \mathrm{Abs} = \left(\frac{\Delta H_{\mathrm{ads}}}{RT}\right) + \ln a + \ln b$$

where a is $\left(\frac{\tau_0}{n_0}\right)$ and b is $\left[\frac{p}{(2\pi mkT)^{1/2}}\right]$; therefore a plot of ln ΔAbs versus $1/T$ is linear with slope equal to $\Delta H_{\mathrm{ads}}/R$ [16].

This model can provide an effective description of adsorption process in many systems, but its disadvantages are that it does not provide a very good description of the process in systems involving physical adsorption and it explicitly forbids adlayers having a value of $\theta > 1$ so it cannot deal with multilayer adsorption. There is also the assumption that the same energy applies to all sites, while in fact most systems will have sites of different energies due to factors such as molecular orientation and other consequences of whatever deposition process was employed [18]. Aggregation may also be a complicating factor. However, using this model and taking results at different temperatures it is possible to arrive at a figure for binding energy.

Binding energy for octaphenyl-di-tert-butylphthalocyanine iron(II)

The binding energy for octaphenyl-di-tert-butylphthalocyanine iron(II) was calculated from temperature studies using the Langmuir model. The change in absorbance during exposure to carbon monoxide gas was monitored with time at five different temperatures, 293, 298, 303, 308, and 313 K (Tables 3, 4, 5, 6, 7 and Fig. 4).

As can be noticed octaphenyl-di-tert-butylphthalocyanine iron(II) thin film shows different response characterization when the temperature was changed.

The following equation was used

$$\ln \Delta \mathrm{Abs} = \left(\frac{\Delta H_{\mathrm{ads}}}{RT}\right) + \ln a + \ln b.$$

Table 3 Absorbance change with exposure time to CO at 293 K

Time (s)	Absorbance	ΔAbs
0	0.4212	0.0000
60	0.4403	0.0191
240	0.4692	0.0480
600	0.5112	0.0900
1200	0.5202	0.0990
1800	0.5367	0.1155
2700	0.5732	0.1520

Table 4 Absorbance change with exposure time to CO at 298 K

Time (s)	Absorbance	ΔAbs
0	0.4192	0.0000
60	0.4304	0.0092
240	0.4573	0.0361
600	0.4853	0.0641
1200	0.4953	0.0741
1800	0.5038	0.0826
2700	0.5293	0.1081

Table 5 Absorbance change with exposure time to CO at 303 K

Time (s)	Absorbance	ΔAbs
0	0.4201	0.0000
60	0.4315	0.0103
240	0.4536	0.0324
600	0.4783	0.0571
1200	0.4872	0.0660
1800	0.5031	0.0819
2700	0.5168	0.0956

Table 6 Absorbance change with exposure time to CO at 308 K

Time (s)	Absorbance	ΔAbs
0	0.4187	0.0000
60	0.4297	0.0085
240	0.4408	0.0196
600	0.4592	0.0380
1200	0.4637	0.0425
1800	0.4695	0.0483
2700	0.4876	0.0664

Table 7 Absorbance change with exposure time to CO at 313 K

Time (s)	Absorbance	ΔAbs
0	0.4196	0.0000
60	0.4221	0.0009
240	0.4376	0.0164
600	0.4501	0.0289
1200	0.4598	0.0386
1800	0.4672	0.0460
2700	0.4756	0.0544

Therefore, by plotting ln ΔAbs against $1/T$ a straight line is obtained with gradient equal to $\Delta H_{\mathrm{des}}/k$, to calculate the binding energy (Table 8).

From the best straight line in Fig. 5 the binding energy for octaphenyl-di-tert-butylphthalocyanine iron(II) in the sol–gel system is 0.401 eV. This is relatively low value for

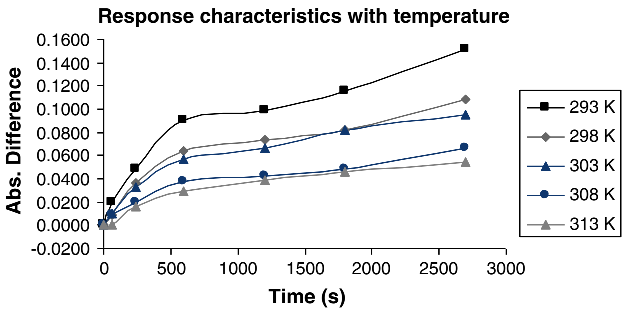

Fig. 4 Response characteristics of thin film at different temperature

Table 8 Binding energy data according to Langmuir model

Temperature (K)	1/(*T*)	ΔAbs	ln ΔAbs
293	0.003413	0.1520	−1.8839
298	0.003356	0.1081	−2.2247
303	0.003300	0.0956	−2.3476
308	0.003247	0.0664	−2.7121
313	0.003195	0.0544	−2.9114

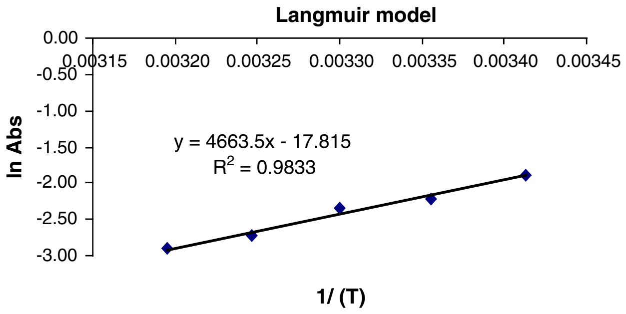

Fig. 5 Plot ln ΔAbs against 1/*T* to calculate binding energy according to Langmuir model

the binding energy, which indicates that the interaction between the gas and the active compound is a weak chemisorption or physisorption [18, 21]. This is desirable from the point of view of an effective practical sensor, since too strong an interaction, such as the reflection of the formation of new covalent bonds with the gas, could give an irreversible effect from which a sensor would not easily recover. This would produce an irreversible indicator device, rather than a reversible sensor. In fact, we find that the optical response to carbon monoxide recovers after some 5 min exposure to ambient air, confirming the facile recovery that is predicted from our binding energy data.

Conclusions

The highly substituted phthalocyanine derivative octaphenyl-di-tert-butylphthalocyanine iron(II) when entrapped in a thin film sol–gel matrix gives a good response to CO, suitable for further study in a device application. The thin film showed a response to 1000 ppm CO gas after 1 min exposure, 10 min for substantial response, and the recovery time was five some minutes in ambient room conditions.

The binding energy for octaphenyl-di-tert-butylphthalocyanine iron(II) entrapped in a sol–gel was calculated and was found to be 0.401 eV, a value that suggests interaction between the gas and the active compound to be weak chemisorption or physisorption. This is a desirable result since it offers a sensor with relatively quick response with fast recovery time, but for a thoroughly effective practical device for optical sensing of carbon monoxide gas, we need to perform further studies on aggregation phenomena of the phthalocyanines, to improve the formation of thinner organic films and to perform a more extensive study on the permeability of these thin films to CO gas.

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