

Sterically hindered phthalocyanines: solution–phase interactions with carbon monoxide

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Abstract Equilibrium measurements for the interaction between various substituted phthalocyanine iron(II) and phthalocyanine (III) and carbon monoxide gas in DMSO are reported. The preparation of a novel octaphenyl-di-tert-butylphthalocyanine iron(II) is described. Variation of the phthalocyanine ring substituents, and the oxidation state of the iron metal, altered the sensitivity of the phthalocyanine towards the carbon monoxide by changing the properties of the ring, especially the tendency towards aggregation and the availability of electron density for binding purposes. Gradual spectroscopic changes were observed for the formation of the complex between carbon monoxide and the phthalocyanine derivatives. The equilibrium constant for octa-phenyl-di-tert-butylphthalocyanine iron(II) is 15170 L/mol and for phthalocyanine iron(III) is 2118 L/mol when compared to the reference phthalocyanine iron(II) value of 7447 L/mol. The results indicate that the sensitivity to carbon monoxide increases with an increase in the electron density on the phthalocyanine ring.

Introduction

The phthalocyanine ring system, in which the highly-conjugated 38 π -electron heterocyclic unit conveys consequent electronic, redox, optical and photochemical properties, offer opportunities for a wide range of applications in molecular electronics, particularly in view of the numerous

possibilities for modification of behaviour by strategic structural manipulation [1, 2]. This is shown in Fig. 1, in which the two internal protons on the nitrogen atoms may be replaced by metals, giving phenomena due to overlap between the metal orbitals and the ligand ring-system orbitals. In addition, the compound also has 16 reactive sites on the peripheral aromatic rings. This allows for the preparation of a great many phthalocyanine derivatives, and the numerous applications for which they have been studied include for example: use as electrocatalysts [3], in the development of high energy density batteries [4], in photodynamic therapy [5] and in gas sensing [6].

Optical carbon monoxide sensors

Our aim is to produce simple, reliable and accurate small-scale devices for the sensing of key gases in the environment, and we have turned our attention to carbon monoxide, a toxic gas with wide scope for unexpected presence in the ambient due to incomplete combustion processes. Carbon monoxide is toxic because it binds to the iron–porphyrin complex in haemoglobin, thereby diminishing oxygen availability to the living organism. As a porphyrin-mimic, iron phthalocyanine has been tested for carbon monoxide sensing [7], but for our application it suffers from considerable drawbacks, namely very poor solubility and miscibility properties, making it difficult to disperse, such that its reactivity towards carbon monoxide iron atoms are unavailable on a microscopic scale to interact with the gas molecules.

In fact, even when apparently dispersed in a solvent or other phase, there is a problem that besets phthalocyanines in many of their promising applications. This is aggregation, in which the close-to-planar rings nestle together to occlude access to the central metal atoms of all but the

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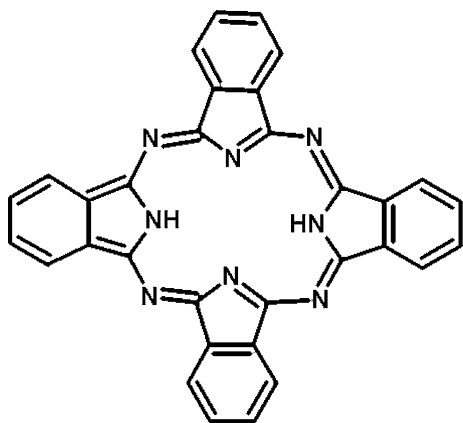


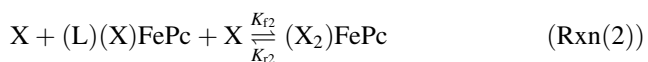
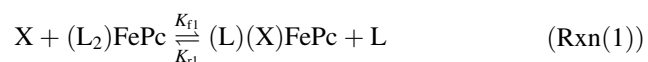
Fig. 1 Phthalocyanine

outermost rings. These non-covalent aggregates may be effectively linear or staggered in aspect, and can be very persistent, even at low phthalocyanine concentrations, and can affect not only desired interactions for the in-service application, but can also influence the purification and characterisation processes of the phthalocyanines during preparation [8].

This study reports on our attempts to minimise deleterious aggregation phenomena, and to quantify the binding of carbon monoxide in solution phase to iron phthalocyanine derivatives that contain bulky sterically hindering groups, this being our strategy not just to modify aggregation effects, but also to enhance solubility and phase-compatibility phenomena, and other physical properties, as well as consequent improvements in sensitivity to carbon monoxide.

Binding constants to phthalocyanines

Various metallophthalocyanines have been widely studied with axially binding species such as oxygen, nitric oxide, cyanide, pyridine, imidazole and carbon monoxide as ligand groups [9–12]. These have different equilibrium and rate constants. One molecule of phthalocyanine can react with one molecule of ligand in the case of NO, O₂ and CO [9], or with two molecules in the case of the CN ion, pyridine and imidazole [12]. Reactions Rxn(1) and Rxn(2) show general mechanisms for reactions of metal phthalocyanine with a ligand in a stepwise process (see below), where L is the leaving group and X is the entering ligand.



Iron (II) phthalocyanine showed the best response to this gas in the optimum solvent, giving a suitable optical change upon complexation [13]. We found that the best solvent for solution-phase studies in our system, especially for our highly sterically hindered materials was dimethyl sulphoxide (DMSO), and also to some extent dimethylformamide (DMF). The main aim of this study is to try to ensure maximum accessibility of the gas to the central metal atom, in order to observe the intrinsic parameters of interaction, and so to better elucidate a system that might be effective in a practical sensor.

Experimental

Materials

Iron (II) phthalocyanine was obtained from Eastman Kodak Co. and used without further purification. The following were purchased from Aldrich and used without further purification: potassium carbonate (99.995%), 4,5-dichlorophthalonitrile (99%), *N,N*-dimethylformamide (99%), dimethylsulfoxide (99%), carbon monoxide (99%), tetraphenylcyclopentadienone (98%), fumaronitrile (98%), benzene (99%), bromine (99%), toluene (99%), bromobenzene reagent (99%), 4-*tert*-butylphthalonitrile, iron (III) phthalocyanine chloride and 1,8-Diazabicyclo[5.4.0]undec-7-ene, 3,3',3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetraol.

Instrumentation

A Shimadzu UV-Visible recording Spectrophotometer UV-2100, a PerkinElmer Lamda 25 UV/Vis spectrometer and an IR Nicolet 210 were used routinely in the laboratory. Other instrumentation was through external analytical agencies: e.g. Exeter Analytical CE 440 elemental analyser, Bruker BioSpin AVANCE III NMR 600 plus 500 MHz and Waters LCT PremierTM XE (TOF) mass spectroscopy.

Synthesis of octaphenyl-di-*tert*-butylphthalocyanine iron(II) (**1b**)

Figure 2 shows the multi-step synthesis used for octaphenyl-di-*tert*-butylphthalocyanine iron (II). For the first step tetraphenylphthalonitrile (**1a**) was synthesised. This is a white powder, confirming that the phenyl rings are twisted out-of-plane, and is thermally stable to its melting point. However, it is not possible to tetramerise this compound in any effective yield, due presumably to ortho-interactions between the outlying phenyl substituents on adjacent

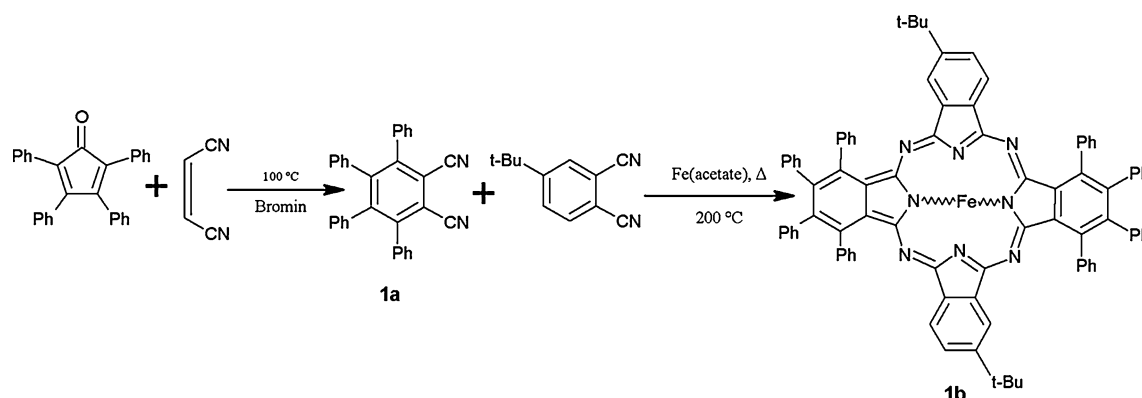


Fig. 2 Multi-step synthesis for Octaphenyl-di-tert-butylphthalocyanine iron(II)

quadrants of the macrocycle **1b** (envisage the two vertical quadrants having four phenyl substituents instead of a single *t*-butyl group). This therefore directs the second step to the symmetrical structure shown. For comparison purposes, the fully *t*-butyl derivative was synthesised (i.e. no tetraphenyl component) all four quadrants have only mono-*t*-butyl substituents.

Synthesis of tetraphenylphthalonitrile (**1a**)

The procedure for the synthesis and purification of this compound has been reported elsewhere [13, 14]. The final yield of white crystalline powder was around 65%. For identification purposes, the melting point of 265.3–265.4 °C agreed with the literature value [14], the ¹H-NMR in CDCl₃ showed an aromatic triplet: doublet combination (43:33), and the mass spectrum showed a strong signal at *m/z* 432. Elemental Analysis gave: found 88.7%C, 4.77%H, 6.24%N; theoretical for C₃₂H₂₀N₂ is 88.86%C, 4.79%H and 6.46%N.

Synthesis of compound (**1b**)

Tetraphenylphthalonitrile (1.2 g, 0.0028 moles), 4-tert-butylphthalonitrile (340 mg, 0.0018 moles) and iron(II) acetate (165 mg, 9.5 × 10⁻⁴ moles) were mixed together and refluxed for 72 h in 20 mL of *N,N*-dimethylethanolamine; five drops of 1, 8-diazabicyclo [5.4.0]-undec-7-ene were added prior to refluxing. The flask was left to cool at room temperature for 30 min before 30 mL of methanol and water (5:1 v/v mixture) were added followed by stirring for 15 min. The solution was filtered under vacuum and the filtrate was washed with methanol. The product underwent a careful purification procedure, using two sequential chromatography columns. The first column silica gel used as stationary phase and eluted with toluene, did not fully separate out individual product fractions, but allowed gross removal of by-products, impurities and

unreacted components. In the second run, silica gel was used as stationary phase and eluted with toluene and hexane (4:1 v/v), three fractions were observed and the second fraction was collected and analysed further. The identification for this compound was performed using mass spectroscopy. A large signal at *m/z* 1288 was found, which corresponds to the molecular weight of this compound. There were some values in mass spectroscopy result which is related to dimer which may be formed during the ionization step in mass spectroscopy.

Determination of the equilibrium constant between phthalocyanine iron (II) derivatives and carbon monoxide in DMSO

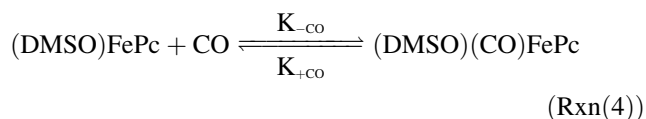
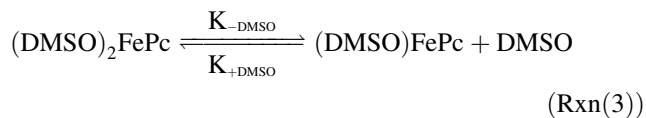
A small amount of the compound (≈ 20 mg) was weighed into a 25.0 mL volumetric flask and dissolved in 25.0 mL DMSO to give solution A. A total of 2.0 mL of solution A was transferred into 7 × 25.0 mL volumetric flasks, numbered from 1 to 7. Different concentrations of carbon monoxide were added to each flask using different volumes of DMSO saturated with carbon monoxide (solubility of CO in DMSO at 20 °C and 1 atm is 1.1 × 10⁻³ mole/L [7]). The solution was kept in a closed system under a CO atmosphere at 20 ± 1 °C.

For all solutions the UV absorbance was taken at the maximum wavelength of the phthalocyanine complex at 670 nm.

Results and discussion

Equilibrium and kinetic studies of the reaction between unsubstituted phthalocyanine iron and carbon monoxide in DMSO solution have been published [7]. The reaction seems independent of temperature over the range studied and stoichiometrically the ratio is 1:1 between iron phthalocyanine and carbon monoxide. The reaction happens

through a dissociative mechanism in which a five coordination intermediate is formed and a study shows that five coordination (DMSO)FePc with iron as metal is more reactive than with other corresponding metals [15]. The overall ligand substitution may be represented by the following specific reaction scheme in reactions Rxn(3) and Rxn(4):



The reaction of substituted phthalocyanine iron (II) with carbon monoxide, which is an axial ligand, was investigated through different aspects. Some of the compounds studied are commercially available such as iron(II) phthalocyanine which is used as a reference in comparative studies. Iron(III) phthalocyanine chloride was used to see the effect of the atom in a higher metal oxidation state and hexadecachlorophthalocyanine iron(II) is used to test polyhalogenated derivatives of the ring system. Other compound was synthesized such as a novel octaphenyl-di-tert-butylphthalocyanine iron(II) (**1b**).

Determination of equilibrium constants

Equilibrium constants for all the compounds were calculated, since the equilibrium constant gives a good estimate of reaction kinetics between phthalocyanine derivatives and carbon monoxide and can provide a measure of the sensitivity to carbon monoxide. It was assumed that the reaction between the carbon monoxide and phthalocyanine can be represented by the reaction Rxn(5) below—the solvent has been removed for simplicity.



where $K_{eq} = K_f/K_r$.

So

$$[FePcCO]/[FePc] = K_{eq}[CO]^n \tag{1}$$

For simplicity, and by assuming that

$$\left(\frac{[FePcCO]}{[FePc]}\right) = \left(\frac{(A - A_0)}{(A_\infty - A)}\right) \tag{2}$$

where A is the absorbance at equilibrium, A_0 is the absorbance of the initial concentration of Pc and A_∞ is the maximum absorbance at which there is no further increase of absorbance with any further addition of carbon monoxide, a final Eq. 2 can be derived:

$$\log\left(\frac{(A - A_0)}{(A_\infty - A)}\right) = \log K_{eq} + n \log[CO] \tag{2}$$

Therefore using different concentrations of carbon monoxide, the absorbance changes can be monitored and a plot of $\log\left(\frac{(A - A_0)}{(A_\infty - A)}\right)$ versus $\log[CO]$ will yield a slope of n, which is the number of molecules of carbon monoxide that react with one mole of phthalocyanine, and an intercept equal to $\log K_{eq}$ [16].

The response to carbon monoxide was examined for all available phthalocyanine iron derivatives. This was performed by adding an accurate volume of DMSO saturated with carbon monoxide to a constant concentration of phthalocyanine iron—see Fig. 3.

In this experiment a comparative study between substituted phthalocyanine compounds and a reference sample, unsubstituted iron (II) phthalocyanine was undertaken. This experiment was repeated several times on different days to confirm reproducibility.

Table 1 shows the equilibrium constants and values for n, for all available phthalocyanine iron derivatives. The n values in all cases are nearly equal to unity indicating that the reaction ratio is 1:1.

Fig. 3 Spectrum of Fe(II) phthalocyanine in DMSO with different concentrations of CO

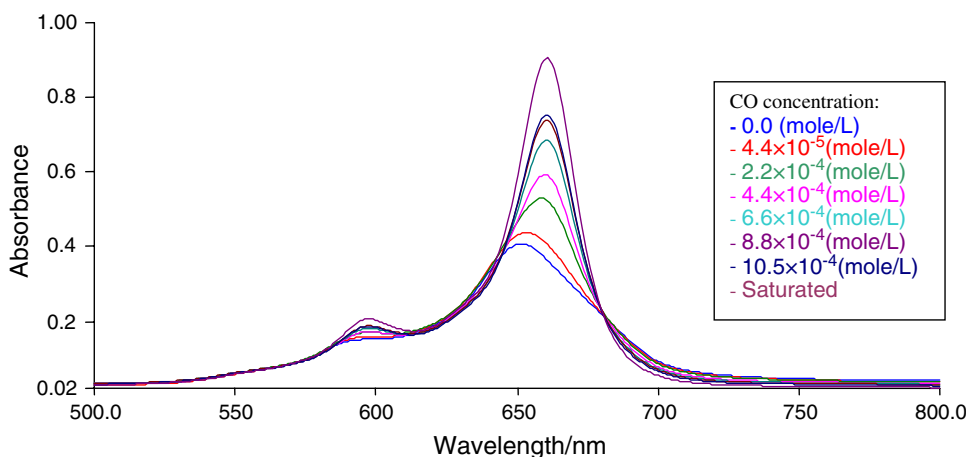
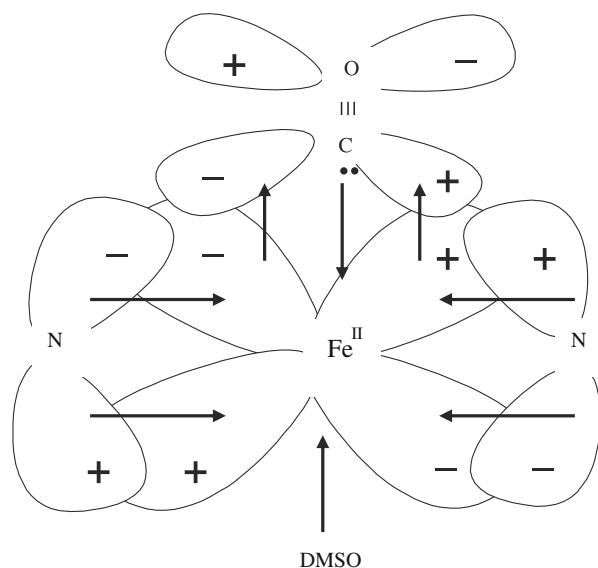


Table 1 Values of equilibrium constant for phthalocyanine iron derivatives and carbon monoxide in DMSO

Compound	$\log K_{\text{eq}}$	$K_{\text{eq(L/mole)}}$	n
Fe(II)Pc	3.872 ± 0.09	7,447	1.094
Fe(III)Pc	3.326 ± 0.04	2,118	1.009
Compound (1b)	4.181 ± 0.10	15,170	1.085
16-Chlorinated PcFe(II)	2.762 ± 0.08	579	0.917

The effect of substituents in solution phase studies was deduced based on electron density considerations, on the phthalocyanine ring and the central iron atom. The nature of the binding between carbon monoxide and the iron atom in phthalocyanine is based on the fact that carbon monoxide is a very weak σ donor and strong π acceptor ligand while iron phthalocyanine acts as a σ donor and π acceptor [17]. Hence when carbon monoxide is bubbled through the solution, the carbon monoxide molecule will withdraw π electron density from the iron atom so that the carbon monoxide molecule will bind with the iron. This will decrease the electron density on the iron which will decrease the ability of the iron to bind to a second strong π acceptor ligand (another carbon monoxide molecule) but will increase the ability of the iron atom for a σ donor (e.g. a DMSO molecule). Thus one molecule of carbon monoxide will react with a molecule of iron phthalocyanine, see Fig. 4. However, the extra stability of the DMSO is gained through π -back bonding from carbon monoxide. So increasing the electron density on the central metal will be

**Fig. 4** Overlapping orbital in (DMSO)Fe(CO)Pc, the arrows represented the direction of electron donation

the key to increase the reactivity to bind with the gas molecule [17].

In iron (III) phthalocyanine chloride, the higher oxidation state has a negative effect on the reaction with carbon monoxide since it decreases the electron density on the iron atom which makes the CO less likely to bind to the metal. The important result from this study is that compound (**1b**) gave the highest value for the equilibrium constant, from which it may be deduced that phenyl groups affect the reaction with carbon monoxide. This may be via two ways. Firstly they decrease the tendency of the molecules to aggregate and secondly they enhance the reaction with carbon monoxide by increasing the electron density on the ring, which increases the ability of the ring to react as a σ donor.

In the commercially available hexadecachlorophthalocyanine iron(II) compound, which was tested for comparison in this study, the chlorine atoms, due to their strong inductive withdrawing effect [18], should decrease reactivity of this compound to carbon monoxide as the inductive effect in polychloroaromatics outweighs the mesomeric effect in this case [19], and this was what we observed.

From our results, octaphenyl-di-tert-butylphthalocyanine iron(II) has the highest equilibrium value of 15170 mole/L which is almost double that of the unsubstituted phthalocyanine iron(II). As a result, our novel compound appears to be more sensitive towards carbon monoxide gas and therefore could be used in various applications for the detection of a wider range of carbon monoxide concentrations.

Conclusions

Iron phthalocyanine has chemical similarities to the active component of the haemoglobin molecule, so it is expected to be reactive towards CO gas.

Octaphenyl-di-tert-butylphthalocyanine iron (II) appeared to be the most sensitive compound to carbon monoxide with an equilibrium constant of 15170 mole/L, which is as predicted since it shows less aggregation in solution and has a greater availability of electron density on the iron atom due to electron donating groups especially in this kind of compound where the phenyl is twisted out of plane so it will have an effect like alkyl group.

Hexadecachlorophthalocyanine iron appeared to be the least sensitive compound with an equilibrium constant of 579 mole/L. This is due to the effect of electron withdrawing groups outweighing resonance donation and so decreasing the availability of electron density on metal/ring system so making the reaction with carbon monoxide difficult.

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