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Interaction studies of carbon monoxide and iron porphyrins in ionic liquids

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ABSTRACT

Air pollution is a serious day-to-day problem faced by the developing and the developed nations in the World. Automobile exhaust is one of the major source of CO emissions, other sources of CO include industrial processes, residential wood burning etc. Areas with heavy traffic congestion generally have higher levels of CO. Carbon monoxide causes harmful health effects by reducing oxygen delivery to different organs and tissues in human body. At extremely high levels, CO can cause death. Thus, harmful effects of CO from automobile exhaust has been a constant cause of concern and thereby necessitate it to be reduced in concentration from automobile exhaust. In the present communication CO binding properties of 5, 10, 15, 20-tetraaryliron(II) porphyrins were examined. The study indicated that the different substituents on the tetraaryliron(II) porphyrin do not have significant effect on the binding affinity of CO in [bmim][PF_6]. Ionic liquid creates an environment that could significantly enhance the binding of CO with TAPFe(II)1-MeIm/[bmim][PF_6].

Keywords: Carbon monoxide, iron porphyrins, automobile exhaust, carboxyhemoglobin.

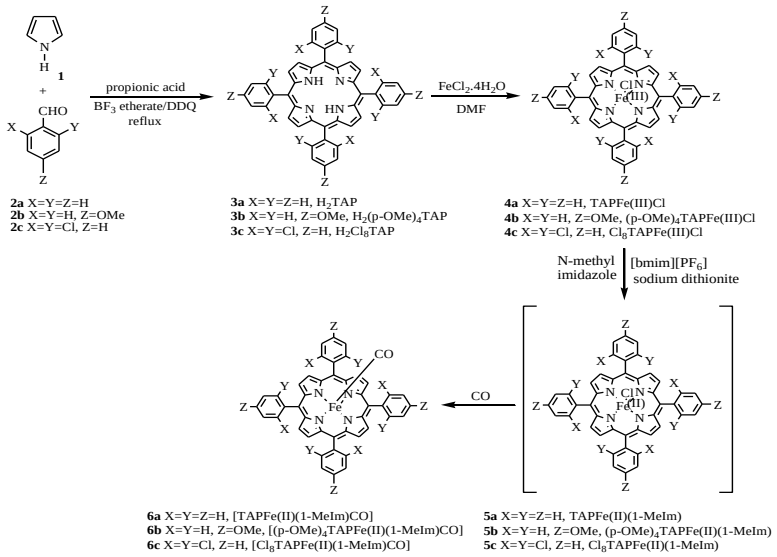
INTRODUCTION

The emissions from motor vehicles are major contributors to air pollution in metropolitan cities like Delhi. Exposure of high levels of CO for short duration in an interior environment may lead to death.[1,2] After breathing in, CO interferes with the cardiovascular system by readily combining with hemoglobin to form carboxyhemoglobin (COHb). The high percentage of COHb causes cardiovascular disease, neurological damage especially in young children.[3-5]

Research done in the field of automobile machines and manufacture comprise of two major fields of work, e.g. increasing the efficiency of fuel consumption and reducing the toxicity of out-coming exhaust.

Thus, there is an urgent need to develop some method to reduce CO emission from automobile exhaust. Metalloporphyrin is a molecule with a metal atom at the center of a porphyrin ring which is an important unit in various biological systems such as haemoglobin.

Iron is present in the central core of hemoglobin which is coordinated with four nitrogen atoms in the porphyrin ring and one nitrogen of the histidine unit of the side chain. The sixth position above the iron atom is empty where small molecules like O_2 and CO binds.[6] The binding affinity of CO to heme is greater than O_2, but it decreases when the heme is embedded in the protein matrix.[7] Thus the nature of the groups attached to the heme pocket and ligands present in the iron coordination sphere modifies the binding affinity of heme in hemoproteins.Room-temperature ionic liquids (RTILs) are effective green solvents for variety of reactions.[8-13] The chemical and physical properties of the ILs can be modified by the choice of reagents according to the need of the reaction.[10-15] Different metalloporphyrins have been used as catalysts to imitate the various reactions of heme enzymes and proteins in ILs.[10,16] To understand the role of different reaction conditions, we have examined the binding of 5,10,15,20-tetraaryliron(II) porphyrins with CO to reduce its emission from automobile exhaust in imidazolium ILs (Scheme 1).



Scheme 1**:** Binding of different aryl substituted *meso*-tetraarylporphyrins with CO inionic liquid.

METHODOLOGY

UV-Visible spectra (λ_{max}, nm) were recorded on Perkin Elmer, Lambda 35 UV-Vis spectrophotometer. Infrared spectra (ν_{max}, cm^{-1}) were recorded on a Shimadzu IR 435 spectrometer. Proton NMR spectra were obtained on a Bruker Avance 300 spectrometer using TMS as internal standard (chemical shift in ppm).

Synthesis of porphyrins

The different iron porphyrins and ILs were synthesized using slightly modified reported procedures.[17,18,19]

Synthesis of 5,10,15,20-tetraarylporphyrins

Benzaldehyde or *p*-methoxy benzaldehyde(0.05 moles) and freshly distilled pyrrole (0.05 moles) were added simultaneously to the refluxing propionic acid and the refluxing was continued for 30 min. The reaction mixture was left at room temperature for 12 h. The glistening purple crystals were filtered, washed with water and methanol,then it was recrystallized from $CHCl_3$:MeOH to get desired product.

5,10,15,20-tetraphenylporphyrin [H_2TAP] (**3a**):UV-Visible ($CHCl_3$, λ_{max} in nm): 417, 510, 548, 589, 649; IR (KBr, cm^{-1}): 3482, 2960, 1642, 1580, 1474, 1442, 1350, 1068; ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 3.02 (s, 2H), 7.70-8.32 (m, 20H), 8.72 (s, 8H).

5,10,15,20-tetra(*p*-methoxyaryl)porphyrin [$H_2(OMe)_4$TAP] (**3b**): UV-Visible ($CHCl_3$, λ_{max} innm): 415, 510, 545, 580, 640; IR (KBr, cm^{-1}): 3472, 2938, 1646, 1585, 1478, 1445, 1350, 1072; ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 2.91 (s, 2H), 3.98 (s, 12H), 7.62-8.12 (m, 16H), 8.82 (s, 8H).

Synthesis of 5,10,15,20-tetra-(2′,6′-dichloroaryl) porphyrin

Freshly distilled pyrrole (5 mmol) and 2,6-dichloro-benzaldehyde (5 mmol) were added to dry $CHCl_3$ (500 mL) with refluxing while constant stirring. The BF_3-ethrate (1.15 mmol) was injected through septum to the above mixture and it was refluxed for 1h. The reaction mixture was cooled and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (38 mmol) was added to it and was refluxed for additional 1 h. After cooling down to room temperature triethylamine (1.15 mmol) was added with stirring. The solvent was evaporated and the residue so obtained was chromatographed over silica gel (60-120 mesh). On elution with petroleum-ether:$CHCl_3$(1:1), 5,10,15,20-tetra-(2′,6′-dichloroaryl)porphyrin (H_2Cl_8TAP) was obtained as purple crystals, which was recrystallized from $CHCl_3$:MeOH in 20% yield.

5,10,15,20-tetra-(2′,6′-dichloroaryl) porphyrin [H_2Cl_8TAP] (**3c**): UV-Visible ($CHCl_3$, λ_{max} in nm): 418.8, 480.2, 512.6, 540, 5.88, 643.6; IR (KBr, cm^{-1}): 3490, 2970, 1670, 1600, 1484, 1355, 1082; ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 2.53 (s, 2H), 7.70 (t, 4H, *J*=7.7 Hz), 7.79 (d, 8H, *J*=7.7 Hz), 8.67 (s, 8H).

Synthesis of 5,10,15,20-tetraarylporphyrinatoiron(III)chloride [TAPFe(III)Cl]

5,10,15,20-tetraarylporphyrin (H_2TAP) (2.44 mmol) and $FeCl_2.4H_2O$ (11.0 mmol) were dissolved in dimethylformamide (200 mL) and refluxed for 3 h. The hot solution was filtered, cooled and dilute HCl was added to it in small portions.

The precipitated complex was separated by filtration and crystallized twice from a mixture of 1,2-dichloroethane and *n*-hexane to get TAPFe(III)Cl in 78% yield.

5,10,15,20-tetraphenylporphyrinatoiron(III)chloride [TAPFe(III)Cl] (**4a**): UV-Visible ($CHCl_3$, λ_{max} in nm): 378, 416, 510, 576, 656.6; IR (KBr, cm^{-1}): 2920, 1830, 1596, 1508, 1440, 1334, 1200, 1175, 1070, 1003, 834, 750, 661; ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 6.36 (s, 12H), 12.22 (d, 8H), 8.08 (br s, 8H).

5,10,15,20-tetra(*p*-methoxyaryl)porphyrinatoiron(III)chloride[(*p*-OMe)$_4$TAPFe (III)Cl] (**4b**): UV-Visible ($CHCl_3$, λ_{max}nm): 378, 417, 508, 586, 659; IR (KBr, cm^{-1}): 2960, 1840, 1606, 1510, 1448, 1340, 1210, 1185, 1080, 1013; ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 4.08 (s, 12 H), 6.95 (br s, 8H), 8.43 (br s, 8H), 8.68 (br s, 8H).

5,10,15,20-tetra-(2′,6′-dichloroaryl) porphyrinatoiron (III)chloride [Cl_8TAPFe(III)Cl] (**4c**): UV-Visible ($CHCl_3$, λ_{max} in nm): 370.2, 418, 509, 584, 642; IR (KBr, cm^{-1}): 2922, 2852, 1827, 1734, 1543, 1428, 1190, 1151, 999, 804, 777, 718; ^{1}H NMR ($CDCl_3$, 300 MHz, δ in ppm): 7.70 (t, 4H, *J*=7.8 Hz), 7.79 (d, 8H, *J*=7.8 Hz), 8.26 (br s, 8H).

In situ preparation of iron(II) porphyrin [Fe(II)TAP] and its binding with CO in [bmim][PF_6]

The Fe(III) porphyrins were reduced to Fe(II) porphyrins by slight modification of reported procedures.[20] The different porphyrins (0.080 mmol) were dissolved in [bmim][PF_6] and reacted with saturated solution of aqueous sodium dithionite solution under nitrogen. After the reduction a solution (0.30 mmol) of 1-methylimidazole (1-MeIm) in 6 mL [bmim][PF_6] was added and stirred for 30 min. Then CO gas (0.6 to 20% in balancing nitrogen) was purged into the reaction mixture for 12 h with constant stirring. The completion of the reaction was monitored by TLC, after completion it was extracted using dichloromethane (DCM) and washed with water. The DCM layer was dried over anhy. Na_2SO_4 and solvent was removed to get purple solid which was purged with nitrogen for 10 min. The compounds were characterized using different spectroscopic techniques.

RESULTS

The cyclocondensation of equimolar amount of pyrrole with aldehyde in propionic acid gave 5,10,15,20-tetraarylporphyrin (**3a**) in moderate yield. Similarly 5,10,15,20-tetra(*p*-methoxyaryl)porphyrin (**3b**) was synthesized and characterized using different spectroscopic techniques. 5,10,15,20-tetra-(2′,6′-dichloroaryl)porphyrin (**3c**)was synthesized by refluxing pyrrole, 2,6-dichlorobenzaldehyde and BF_3-etherate in dry $CHCl_3$ followed by the addition of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) to the cooled reaction mixture (**Scheme 1**). Different porphyrins so obtained were reacted with ferrous chloride in dry DMF to give corresponding porphyrinatoiron(III)chloride [TAPFe(III)Cl]. Structure of different TAPFe(III)Cl was confirmed by IR, UV and other spectroscopic data.

The different TAPFe(III)Cl (**4a-c**) were reduced to TAPFe(II)(1-MeIm) (**5a-c**) using sodium dithionite in [bmim][PF_6] *in situ*. The purging of CO into the reaction mixture at ambient temperature for 2 h gave **6a** in 10% yield(Table 1). The yield of **6a** was substantially increased to 90% on increasing the reaction time to12 h (Table 1).

Further an increase in the amount of CO from 2 to 3 equivalents reduced the reaction time and increased the yield of [Fe(TAP)(1-MeIm)CO] (**6a-c**) complex. The reaction of CO with **5a** proceeds more effectively in different ILs as compared to organic solvents (Table 1). Similar results were obtained with other metalloporphyrins (**5b** and **5**

DISCUSSION

The structure of **3a** was confirmed by different spectroscopic data. The UV-Visible spectrum of **3a** indicated the bands at 417, 514, 545, 589 and 652 nm in $CHCl_3$. A singlet at -3.02 ppm for the internal NH protons and a singlet at 8.72 ppm for *β*-pyrrolic protons were observed in the ^{1}H NMR spectrum of **3a**. The phenyl protons appeared as a multiplet between 7.19-7.70 ppm respectively.Further the metallation of porphyrins (**4a-c**) was confirmed using UV-Visible spectroscopic. The UV-Visible spectrum of **4a** showed bands at 416, 510, 576 and 656.6 nm in $CHCl_3$. The UV-Visible spectrum of metallated

porphyrins (**4a-c**) consists of a Soret band with only two Q-bands as compared to four bands present in un-metallated porphyrin (Table 2).

Table 1: Effect of solvent on the binding of CO with [Fe(TAP)(1-MeIm)] (5a).

Entry	Solvent system	Time (h)	% Yield[d]
1.	Toluene	24	80
2.	DCM	12	20
3.	Methanol	24	76
4.	Toluene:methanol (1:1)	20	78
5.	[bmim][PF_6]	2	10
6.	[bmim][PF_6]	12	90
7.	[bmim][BF_4]	12	86
8.	[bmim][Br]	18	80

[d]Isolated Yields; DCM= Dichloromethane; [bmim][BF_4] =butyl methyl imidazolium-bromide; [bmim][BF_4]= butylmethylimidazolium-tetraboroflourate;[bmim][PF_6]=butylmethylimidazoliumhexa flourophospahte

Table 2:UV-visible spectra of different aryl substituted *meso*-tetraaryl iron porphyrinsin [bmim][PF_6].

Entry	Porphyrins	UV-Visible spectra (nm)
1.	TAPFe(III)Cl (**4a)**	416, 510.0, 576.0, 656.6
2.	TAPFe(II)(1-MeIm)$_2$(**7a**)	425, 534, 561
3.	TAPFe(II)1-MeIm(CO) (**6a**)	421, 540
4.	*p*-(OMe)$_4$TAPFe(III)Cl (**4b**)	417, 508, 586, 659
5.	*p*-(OMe)$_4$TAPFe(II)(1-MeIm)$_2$(**7b**)	419, 511, 687
6.	*p*-(OMe)$_4$TAPFe(II)1-MeIm(CO) (**6b**)	424, 538, 695
7.	Cl_8TAPFe(III)Cl (**4c**)	418.4, 509, 584, 642
8.	Cl_8TAPFe(II)(1-MeIm)$_2$(**7c**)	420, 542, 688
9.	Cl_8TAPFe(II)1-MeIm(CO) (**6c**)	423, 513, 694

Further the binding of **5a** with CO in the presence of 1-MeIm in ILs results in the formation of [Fe(TAP)(1-MeIm)CO] that was confirmed by the appearance of the bands at 420 nm and 540 nm in the UV-Visible spectra and the C-O stretching peak in the IR spectrum at 1972 cm^{-1} (Table 2).[21] Similar results were observed with other metalloporphyrins **5b** and **5c** (Table 2). The Soret and Q bands in **4a** were shifted to 425 and 534, 561 nm on addition of the organic bases such as 1-MeIm in excess, due to the formation of [**7a**, Fe(TAP)(1-MeIm)$_2$](Table 2).The effect of ILs in the CO binding with **5a** was also studied by the addition of increasing concentration of [bmim][PF_6] into DCM. The binding of CO with **5a** was slow in DCM, it was markedly enhanced when [bmim][PF_6] was added to DCM (Table 1). This can be attributed to the fact that IL creates an environment by either changing the solvation in the binding site or by stabilizing the charge separation that could significantly enhance the binding of CO with TAPFe(II)1-MeIm/[bmim][PF_6].[22] The metalloporphyrins bearing electron-donating groups (**4b**) and electron withdrawing groups (**4c**) on the phenyl ring do not have any significant role on the binding affinity with CO (Table 3).

Table 3: Effect of different substituentson the binding of *meso*-tetraaryl iron porphyrins [TAPFe(II)(1-MeIm)] (**5a-5c**) CO in [bmim][PF_6].

Entry	System	% Yields[e]
1	TAPFe(II)(1-MeIm)	90
2	(*p*-OMe)$_4$TAPFe(II)(1-MeIm)	92
3	Cl_8TAPFe(II)(1-MeIm)	88

[e]Isolated Yields

CONCLUSIONS

The CO binds with tetraaryliron(II) porphyrins. Different substituents on the tetraaryliron(II) porphyrins do not have very significant effect on the binding affinity of CO in [bmim][PF_6]. An increase in the concentration of ILs in DCM enhances the CO binding indicating the role of ILs in binding. Ionic liquid creates an environment that could significantly enhance the binding of CO with TAPFe(II)1-MeIm/[bmim][PF_6].

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