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LETTER

Preparation and characterization of poly(siloxane)-supported metalloporphyrins: the effect of the support on the electronic absorption spectra

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Preparation and characterization of several supported metalloporphyrins are known, and have been evaluated as electrocatalysts for redox reactions [1–6]. The support used was either the electrode itself or a polymer coating modification of the electrode surface. Modified organic polymer surfaces have also been reported as supports for metalloporphyrins [7, 8]. In our search for new supported catalysts for olefin oxidation reactions, we have employed halogenated poly(siloxane) surfaces [9a] $\text{Sil-}(CH_2)_3X$, as supports for the metalloporphyrin catalyst, $[Mn^{III}(TPyP)]$. Quaternization reactions have been used to bind the $[Mn^{III}(TPyP)]$ species to the surface [9b]. We now report our studies of the effect of support on the electronic absorption spectra of several supported metalloporphyrins [M(TPyP)].

Experimental

Metal salts and other chemicals used in the syntheses were purchased from Aldrich in a pure form. Organic solvents were purified prior to use according to standard methods [10]. Electronic absorption spectra of the metalloporphyrins were recorded on Varian Cary 2300 and/or Hitachi 110 spectrophotometers.

The halogenated polysiloxane was prepared as previously described [9]. The Finkelstein reaction technique was employed to prepare $(MeO)_3Si(CH_2)_3I$ from $(MeO)_3Si(CH_2)_3Cl$ as reported [10]. Iodization was confirmed by grating IR spectral analysis. The metalloporphyrins $[Zn^{II}(TPyP)]$, $[Mn^{III}(TPyP)]^+X^-$ and $[Fe^{II}(TPyP)]$ were prepared by refluxing 5,10,15,20-tetra(4-pyridyl)-21H,23H porphyrin with ten-fold excess of the metal acetate (Zn^{II}) or sulfate Mn^{II} or Fe^{II}) in DMF. The products were purified by chromatography on neutral alumina (Bio-Rad AGF, 100–200 mesh) using $MeOH+CHCl_3$ (5:95 vol./vol.) as eluent as described elsewhere [11–15]. The spectra were measured and compared to literature values (Table 1).

Supported metalloporphyrins were prepared by heating (70–90 °C) stirred mixtures of the halogenated poly(siloxane) with the metalloporphyrin in the proper solvent. The experimental conditions for each preparation are given in Table 2. The resulting solid was then isolated, washed several times with the same solvent and then with acetone before drying. Weight percentages of metalloporphyrins onto supports were measured spectrophotometrically, by subtracting the amounts of unreacted [M(TPyP)] from starting amounts.

Solid state electronic spectra of Ia, Ib, II and III were measured as KBr pellets; the results are given in Table 1. Quaternization was confirmed by treating the supported complexes as ion-exchange columns, through which aqueous $NaNO_3$ solutions were passed. After elution with H_2O, the eluate was treated with aqueous $AgNO_3$ solutions. Precipitation of AgX(s) confirmed quaternization, since it is the only source of X^- ions (Scheme 1). Direct quantitative analysis, for the eluate X^- ions by chloridimetric methods, and/or indirect analysis for precipitated AgX(s) by inductivity coupled plasma emission spectrometry, were carried out to determine the degree of quaternization (*DQ*) (Table 2), viz. *DQ* equals mole X^- per mole [MTPyP]. Direct analysis of eluate Cl^- ion concentration was also done employing a Cobas Mira (Roche) analyser at the National Hospital Laboratories, Nablus, West Bank. Supported metalloporphyrins were also analysed using solid state FT-IR spectra (KBr pellets).

Results and discussion

Metalloporphyrins, [M(TPyP], were supported on halogenated polysiloxane surfaces by the quaternization reaction shown in Scheme 1. Heating at 70–90 °C for 24–72 h gave satisfactory results whereas overheating (*c.* 150 °C) caused decomposition of the

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TABLE 1. Spectral data for solution and solid state metalloporphyrins

Entry number	Metalloporphyrin	Electron absorption spectra (nm) (ϵ (M^{-1} cm^{-1}))			State, solvent[a]	Reference
		λ_{Soret}	λ_{Q1}	λ_{Q2}		
1	$[Zn^{II}(TPyP)]$	424(512×10³)	559(19.4×10³)		solution, $CHCl_3$	19
2	$[Zn^{II}(TPyP)]$	428	561	600	solution, CH_2Cl_2/pyridine	16
3	$[Zn^{II}(TPyP)]$	445	568	608	solid film	16
4	$[Zn^{II}(TPyP)]$	429(325×10³)	523(23×10³)	565(9.4×10³)	solution, pyridine	18
5	$[Zn^{II}(TPyP)]$	428	560	600	solution, DMF	[b]
6[c]	$[Zn^{II}(TMPyP)]^{4+}$	436(168×10³)	562(16×10³)	602	solution, H_2O	17, 20
7	$[Zn^{II}(TMPyP)]^{4+}$	442	564	605	solid film	16
8[d]	$[Zn^{II}(T(Oct.)PyP)]^{4+}$	423	559	606	solution, H_2O	21
9	Ia	448.8	571	616	solid, KBr pellet	[b]
10	Ib(i)	428	562	609	solid, KBr pellet	[b]
11	Ib(ii)	432			solid film	[b]
12	[Zn(TPyP)]	450	563	604	solid, mixed with Sil–I in KBr pellet	[b]
13	[Zn(TPyP)]	440	566	600	solid, mixed with Sil–Cl in KBr pellet	[b]
14	$[Mn^{III}(TPyP)]^{+}$	474(80×10³)			solution, toluene	13
15	$[Mn^{III}(TPyP)]^{+}$	463(85×10³)			solution, EtOH	13
16	$[Mn^{III}(TPyP)]^{+}$	463(90×10³)			solution, H_2O	13
17	$[Mn^{III}(TPyP)]^{+}$	465(95×10³)	563(51×10³)		solution, HCOOH	18
18	$[Mn^{III}(TPyP)]^{+}$	466	570	612	solution, DMF	[b]
19	$[Mn^{III}(TMPyP)]^{5+}$	463(96×10³)	506	562	solution, H_2O	13, 17, 20
20[d]	$[Mn^{III}(T(Oct.)PyP)]^{5+}$	463	560	590	solution, MeOH	21
21	$[Mn^{III}(TMPyP)]^{5+}$	463	506	562	solid film	20
22	$[Mn^{III}(TMPyP)]^{5+}$	463	507		colloid	20
23	II	466	566		solid, KBr pellet	[b]
24	III	414	525	570	solid, KBr pellet	[b]
25	$[Fe^{II}(TPyP)]$	410	520	630	solution, HCOOH	[b]
26	$[Fe^{II}(TPyP)]$	423	529	563, 603, 648	solution, pyridine	19
27	$[Fe^{III}(TMPyP)]^{5+}$	456	575	619	solution, H_2O (pH = 14)	25
28	$[Fe^{III}(TMPyP)]^{5+}$	400			solution, H_2O (pH = 1)	26
29	$[Fe^{III}(TMPyP)]^{5+}$	422	580	630	solution, H_2O (pH = 7)	27

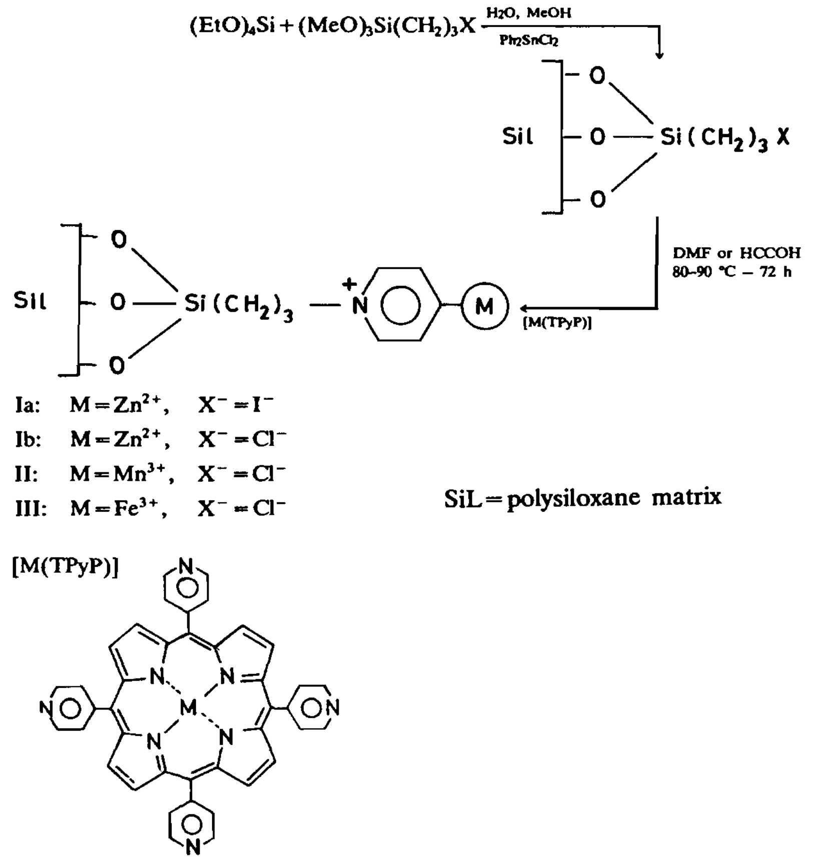
[a] Sil–Cl, chlorinated polysiloxane; Sil–I, iodinated polysiloxane. [b] This work. [c] $[Zn(TMPyP)]^{4+}$ = tetrakis(*N*-methyl-4-pyridyl)porphyrin zinc(II). [d] $[Zn^{II}(T(Oct.)PyP)]^{4+}$ = tetrakis(*N*-octyl-4-pyridyl)porphyrin zinc(II); $[Mn^{III}(T(Oct.)PyP)]^{4+}$ = tetrakis(*N*-octyl-4-pyridyl)porphyrin manganese(III).

TABLE 2. Experimental conditions and analytical data for the supported metalloporphyrins

Sample number	Metalloporphyrin used	Weight (g)	Solid surface	Weight (g)	Solvent	Volume (ml)	*T* (°C)	Time (h)	[M(P)] (wt.%)	*DQ* (moles X/mole [M(P)])
Ia	[Zn(TPyP)]	7.2×10^{-3}	Sil–I	3.8	DMF	21	75	24	0.1236	3.1
Ib(i)	[Zn(TPyP)]	4.7×10^{-3}	Sil–Cl	5.1	DMF	23	72	72	0.063	1.1
Ib(ii)	[Zn(TPyP)]	4.7×10^{-3}	Sil–Cl	1.0	$CHCl_3$	10	63	24		
II(i)	$[Mn(TPyP)](SO_4)_{1/2}$	19.7×10^{-3}	Sil–Cl	5.3	DMF	10	80	72	0.2441	2.2
II(ii)	$[Mn(TPyP)](SO_4)_{1/2}$	20×10^{-3}	Sil–Cl	3.5	DMF	10	80	72	0.5	2.0
III	$[Fe(TPyP)](SO_4)_{1/2}$	13×10^{-3}	Sil–Cl	2.0	DMF	20	80	72	0.65	

metalloporphyrin. Electronic spectra of the supported complexes, with well defined Soret (B) and (Q) bands (Fig. 1) clearly indicate the presence of the metalloporphyrins on the surfaces (Table 1).

For [Zn(TPyP)] it appears that the electronic spectra of I occur at wavelengths higher than those of the solution counterpart spectra (Table 1). This is more pronounced in Ia and to a lesser extent in Ib. These results are consistent with results reported by Takahashi *et al.* [16], with a high red shift for solid [Zn(TPyP)] compared to the solution counterpart spectrum (Table 1). This is attributed to intermolecular interactions between [Zn(TPyP)] molecules. Such interactions are more likely to occur



Scheme 1.

in the solid state. In our supported [Zn(TPyP)], such interactions may occur at the surface causing the red shift. The higher red shift in Ia than in Ib could be due to the higher tendency for intermolecular interactions in Ia. This is presumably due to higher concentrations of [Zn(TPyP)] in Ia (Table 2), which may allow more proximity interactions between neighbouring metalloporphyrin molecules. Higher concentrations in Ia are presumably due to the quaternization reaction being faster with the C–I group than with C–Cl [23, 24].

For [Mn^{III}(TPyP)] the solid state spectra of II resemble solution counterpart spectra (Table 1) with only a slight red shift. This was obvious even with relatively high concentrations of [Mn^{III}(TPyP)] on the support, Table 1. These observations are consistent with other reports. Shimidzu and co-workers [20] reported that solid and colloidal [Mn^{III}(TPyP)] spectra resemble solution counterpart spectra more than for the case of [Zn(TPyP)], which showed higher red shift patterns. The reasons behind the red shift pattern in I and II could not, therefore, be exclusively restricted to [M(TPyP)] intermolecular interactions, as reported for other organic polymer-supported porphyrins [22]. The polarity change of the surrounding matrix may also be responsible for the red shift pattern [20].

Further evidence in support of this discussion is shown in Table 1 (entries 12 and 13). Equimolar amounts of solid [Zn(TPyP)] were thoroughly mixed with solid surface material Sil-$(CH_2)_3X$ (X = I or Cl), to make KBr pellets of the porphyrin–surface mixture without quaternization. The two [Zn(TPyP)] samples showed different spectral patterns with the one in entry number 12 showing higher red shift. The only difference between samples in entries 12 and 13 is the nature of the poly(siloxane) matrix.

Preparation of supported [Fe(TPyP)] on chlorinated poly(siloxane) (III) has also been attempted. The wt.% and *DQ* are shown in Table 2. The solid state spectra of III were conclusive and showed all the characteristic bands of Soret (B) and (Q) regions, Table 1. Unlike the case with Ia and Ib, there is no significant red shift in the spectra of [Fe^{III}(TPyP)] when supported. The red shift here is even smaller than in the case of II.

Catalytic studies employing I, II and III are in progress. Preliminary investigations show remarkable catalytic efficiency in the oxidation reactions of cyclohexene and styrene, with high turnovers (up to 3000).

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