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Coordination Chemistry Reviews
190–192 (1999) 29–45

COORDINATION CHEMISTRY REVIEWS

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Rapid derivatization of mesoporous thin-film materials based on Re(I) zinc-porphyrin 'molecular squares': selective modification of mesopore size and shape by binding of aromatic nitrogen donor ligands

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Accepted 17 February 1999

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PII: S0010-8545(99)00062-4

Abstract

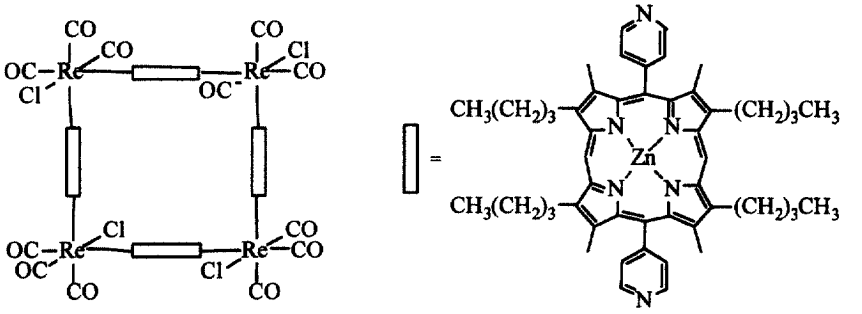
Molecular materials based on thin films of the zinc-containing tetraporphyrinic square assembly, **1**, can be rapidly and, in many cases, completely functionalized by exposure to aqueous or alkane solutions of good N-donor ligands such as pyridine and imidazole. Modification can also be achieved via direct vapor-phase exposure of films to volatile ligands. In both experiments modification is a consequence of simple Zn(II) coordination chemistry and is facilitated by the exceptional mesoporosity of the parent material. Vapor-phase quartz crystal microbalance experiments indicated an average ligand/component square binding stoichiometry of 2.5, in fair agreement with the stoichiometry of **4** implied by absorbance measurements and expected from the number of Zn(II) sites per assembly. Systematic studies with **9** of the more than 40 total ligands examined, show that ligand binding strength is controlled by both ligand basicity (σ electron donating ability) and ligand solvophobic phenomena. In several instances the film modification chemistry was found to be reasonably persistant; in a few instances the modification was demonstrably permanent. For modified mesoporous films in contact with liquid environment, kinetic stability could be qualitatively correlated with thermodynamic stability, as indicated by binding constants. Kinetic stability under these conditions, therefore, is a function of both ligand–N/Zn(II) bond strength and ligand solvophobic character. For films in contact with an inert atmosphere (air), kinetic stability could be correlated successfully with simply the ligand–N/Zn(II) bond strength (as inferred from the ligand pK_a). The combined results support the notion that mesopore derivatization—leading to systematic alteration of component cavity size, shape, and chemical affinity—can be usefully achieved via axial ligation of metalloporphyrins. We suggest that the ready availability of an extended array of derivatized thin film materials could be useful in membrane-based transport applications, catalyst applications, and/or chemical sensing applications.

Keywords: Metallacycles; Mesoporosity; Nanostructues; Supramolecular chemistry

1. Introduction

Neutral molecular squares based on octahedral $Re^{I}(CO)_3(Cl)$ corners with difunctional bridging ligands *cis* to one another have been prepared with a variety of bridging ligands [1,2]. The size of the square cavity, defined by the Re···Re distance, can easily be varied by using bridging ligands of different lengths. The synthetic chemistry is straightforward, the primary requirement being that the bridging ligand be rigid with two coordination sites positioned at ca. 180° angle with respect to one another. Some of the rhenium squares, as well as related rectangles and squares generated with other metals, have been shown to function as molecular hosts in solution-phase host/guest assemblies [3–9]. The host/guest behavior suggests eventual molecular-recognition-based chemical sensing applications for the compounds. Several of the non-porphyrinic Re(I)-containing molecular squares [1,10], as well as other cationic squares [11–14] and rectangles [9] have shown a propensity to form infinite, one-dimensional, zeolite-like channels or pores when assembled in single crystal form. Furthermore, we have recently observed that thin films of the molecular materials with pyrazine, 4,4′-bipyridine, and 4,4′-

bis(pyridyl)ethylene bridges permit transport of molecules smaller than the size of the square cavity, but are blocking toward molecules larger than the component metallocycle's dimension [10]. Molecular size cutoffs corresponding to those expected from Re···Re distances determined from X-ray diffraction or molecular modeling, combined with the observation that thin films of the corresponding $Re(CO)_3(Cl)(L)_2$ 'corners' are much less porous and do not exhibit size discrimination, led us to conclude that the presence of cavities in the squares plays a central role in the observed molecular sieving (i.e. transport in thin films occurs primarily via passage through the square molecules, rather than through intermolecular interstices). Quantitative transport studies show that the molecular-square-derived materials are ca. 10-fold more permeable than related cationic metallopolymeric materials displaying similar permeant size cutoffs [15,16]. The substantially enhanced transport characteristics in the square-derived materials have been attributed to the absence of charge-compensating (channel blocking) counter ions.



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The largest $[Re(CO)_3(Cl)(\mu\text{-}L)]_4$ compound prepared to date (**1**) features a dipyridyl bridging ligand (Zn-porphyrin (Zn-5,15-Py_2P) = 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl)-Zn-porphyrin), with a Re···Re distance of ca. 20 Å [2]. Although a crystal structure of this square is not available, film permeation studies on **1** imply the existence of extended mesopores or channels in the solid state [17]. The size cutoff for molecular transport through the material is consistent with an estimated minimum van der Waals cavity diameter of ca. 18 Å [17]. As shown elsewhere, derivatization of (**1**) via the methods described here either block permeation, or reduce the permeation size cutoff in a fashion consistent with the estimated dimensions of the resulting intrasquare cavity(ies) [17]. Thus, the sharp permeant size cutoff data strongly suggest that molecular transport occurs chiefly through nanometer scale cavities rather than through much larger defects. In the current study, we reasoned that the large cavity sizes and the exceptional mesoscale porosity of thin films of **1**, together with the presence of four potential ligation sites (Zn ions) per square unit, could provide a basis for systematic pore derivatization—including control over component cavity size,

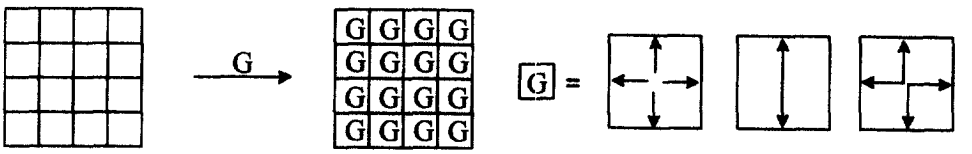
shape, and chemical affinity. In principle, the proposed derivatization could be achieved either by preparing a host/guest assembly in solution, prior to film casting, or alternatively, by modifying the $[Re(CO)_3(Cl)(Zn\text{-}5,15\text{-}Py_2P)]_4$ compound following film casting. The second method, illustrated in Scheme 1, is in many respects, more attractive: it allows for the rapid preparation of an array of modified materials under conditions where the performance of the parent material has already been optimized (e.g. pinhole defect densities have been minimized, molecular porosity has been maximized, etc.). The availability of a large number of derivatized materials would clearly be highly advantageous for eventual array-based or pattern-based chemical sensing applications. It also could prove useful in membrane-based transport applications and novel film-supported catalyst applications.

In this paper, we wish to report on the rapid derivatization of thin films of **1** by uptake of nitrogen-donor guest molecules following film preparation. More than 40 candidate guests or ligands have been examined. The chemical, structural, and electronic factors governing film/ligand complex formation have been determined, as have the primary factors responsible for subsequent kinetic stabilization. We find, for several ligands, that film derivatization is sufficiently efficacious and sufficiently permanent to validate the concept and encourage further investigation.

2. Experimental

2.1. Materials and film preparation

Complex **1** was prepared as previously described [2]. Zn-*meso*-tetra(4-*N*-methylpyridyl)-porphyrin chloride was purchased from Porphyrin Products (Logan, Utah). All guest molecules and solvents were obtained from Aldrich or Lancaster. Films used for the electronic spectroscopy experiments were prepared on glass slides previously washed in a concentrated hydrogen peroxide/sulfuric acid mixture. Thin films were obtained by slow evaporation of a few drops of a chloroform solution of the square, and allowed to dry for at least 30 min prior to use. Drying was necessary to ensure strong adhesion of the film to the glass surface. Based on the average absorbance obtained for dissolved films in chloroform, the molar extinction coefficient for **1**, the film area, and the approximate dimensions of the molecular square ($28 \times 28 \times 18$ Å), and assuming the most dense estimated packing for the squares, film thicknesses were estimated to be on the order of a few tenths of a micron.



Scheme 1.

2.2. Thin film binding and ligand release studies

Films of **1** were modified in water or hexane by adding a few drops of a saturated solution of the guest in the same solvent. In cases where the guest is not soluble in hexane, and uptake from water does not take place, the film can be modified by adding a few drops of a concentrated acetone solution of the guest in hexane. For the limited set of pyridines used in the more quantitative studies, guest uptake is usually complete in about 2 min. Binding constants for the different pyridines in thin film materials were determined in water by gradually increasing the ligand concentration to 1–5 mM. In the case of 4-phenylpyridine, the ligand was added from acetone. (4-Phenylpyridine cannot be added from water, due to its low solubility in that solvent.) Care was taken not to exceed an acetone:water ratio of 1:80 so as to avoid undesired solvent effects. The binding constant for 4-aminopyridine, which possesses an amino nitrogen which can protonate, as well as a pyridinic nitrogen, was measured both in unbuffered water, and in a pH 10 buffer (Fisher Scientific). No dramatic difference in binding constant was observed upon buffering.

Quantitative ligand release experiments, in water, were generally conducted with films that had previously been allowed to uptake the guest molecule from aqueous solution for ca. 30 min. Release was monitored by recording an absorption spectrum in pure water at regular time intervals, with the water being replaced when no further change was detected in the position of the Soret band with time. The procedure was repeated until the Soret band showed no further shift upon rinsing. The absorption maximum of the Soret band usually returned to within 2 nm of its original value (unbound Zn-porphyrin). For vapor phase ligand release studies, films of **1** were exposed to the nitrogen donor guest for 30 min, after which time the guest source was removed. Quartz crystal microgravimetry (QCM) was also used to measure uptake and release of the imine ligands in the vapor phase. The technique is discussed in recent reviews [18,19]; see Ref. [20] for additional details.

2.3. Aqueous solution binding studies

Solution-phase binding studies with the water-soluble compound, Zn-*meso*-tetra(4-*N*-methyl-pyridyl)-porphyrin, were effected using absorption spectroscopy (Hewlett Packard diode array spectrophotometer, model 8452A). The binding constant for 4-picoline was corroborated via spectrofluorometry (Spex Fluorolog 3, emission at 630 nm), where the intensity of luminescence of the porphyrin decreases, as expected [21], upon axial binding of the imine to the Zn atom. Luminescence data were recorded for both a fixed excitation wavelength at 560 nm for all additions of the guest solution, and by following the excitation profile absorption maximum which shifted red slightly upon binding.

3. Results

3.1. Film derivatization (condensed phase)

Graphical summaries of all candidate ligands evaluated are presented in Charts I and II. The positions of the absorption maxima for the three most intense transitions in derivatized films are listed in Table 1. Uptake from water is possiblefor poorly to moderately water-soluble ligands, but not for guests which are highly soluble in aqueous medium, such as imidazole, 1-methylimidazole, or pyridines bearing carboxylic acid or amine groups. If the guest is soluble in hexane, uptake from this solvent is also possible. Guests which are poorly soluble in hexane

Chart I

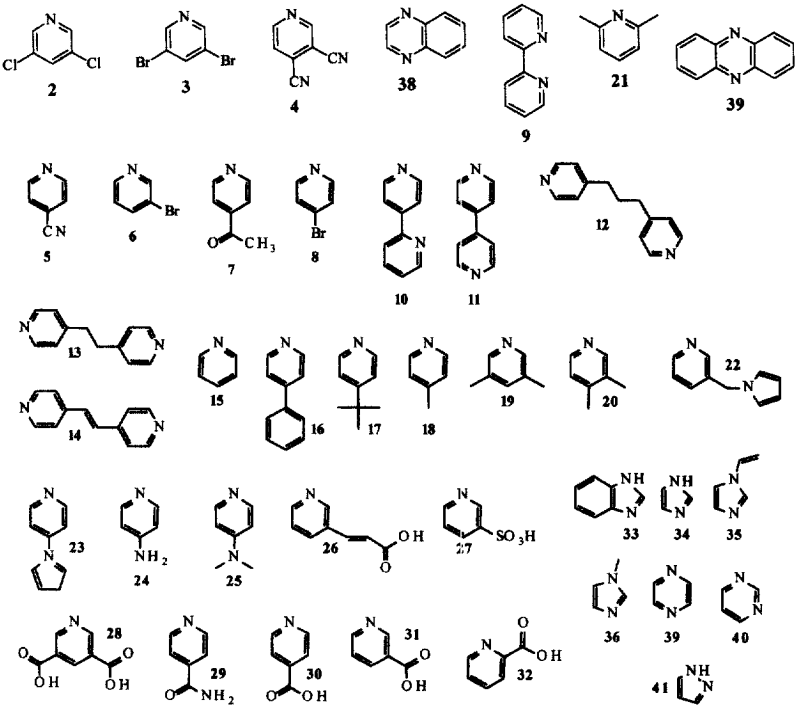
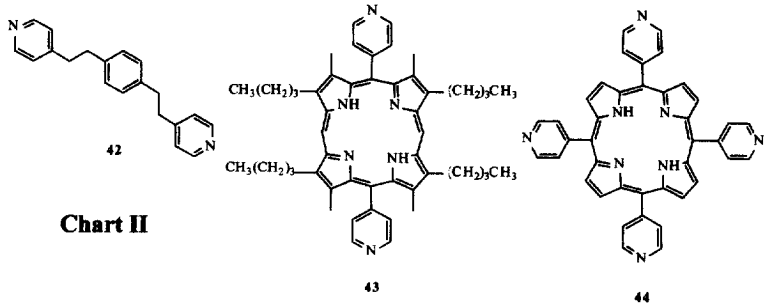


Chart II



or water may be incorporated in thin films by adding the ligand as a concentrated solution in acetone to a film in hexane or water. Chart I lists the guest molecules which showed no binding within the films.

The absence of binding can be rationalized either on a steric basis (i.e. the presence of substituents in the π-position of the coordination site precludes binding), or via electronic considerations (i.e. the Zn(II)–N bond strength of pyridines is known to correlate with the pK_a of the N atom, which reflects the electron density at the donor site). (The pK_a value reported is that for the ligand's conjugate acid in water [22–32]; see Table 1 for details.) Hence, 2,6-lutidine (**21**), which features a pair of π-substituents, shows no detectable binding. Similarly, 2,2′-bipyridine (**9**), which should be incapable of presenting a geometry suitable for axial binding to the Zn-porphyrin, also fails to ligate. On the other hand, although 3,5-dichloropyridine (**2**), 3,5-dibromopyridine (**3**), and 3,4-dicyanopyridine (**4**) all have suitable geometries, none show appreciable binding, consistent with the demonstrably poor electron-donating capabilities (pK_a values for **2** and **3** are 0.67 and 0.82, respectively). No film binding is observed for quinoxaline (**37**) and phenazine (**38**), two potential ligands characterized by both steric hindrance and low electron density on the nitrogen donor atom (pK_a values of 0.56 and 1.2, respectively).

Essentially all sterically accessible pyridines and imidazoles of sufficient base strength (pK_a > ca. 2) can be used to derivatize films of the squares. Derivatization is accompanied by absorption band energy shifts that increase with increasing ligand basicity, as reported previously for solution studies with Zn-tetraphenylporphyrin and other metalloporphyrins [33]. Table 1 also compares the positions of the absorption bands obtained with derivatized films with the shifts observed for **1** in chloroform solution in the presence of 50 ± 10 mM of the ligand. The comparison was made in order to establish whether the shifts observed in the film studies corresponded to ligation of all available Zn sites, or only a fraction. Pyridine and imidazole derivatives with moderate pK_a values, which have hydrogen bonding groups, such as 3-pyridinesulfonic acid, benzimidazole, and those featuring carboxylic acid substituents (see Table 1), show only moderate uptake as evidenced by smaller than expected shifts in porphyrin-based absorbance wavelength.

3.2. Film derivatization (vapor phase)

Vapor phase derivatization can also be accomplished if the candidate ligand is sufficiently volatile. For example, based on absorption spectroscopy, we find that pyrazine, 4-cyanopyridine, 3-bromopyridine, pyridine, and 4-picoline vapor can all be used to derivatize the films in minutes. Further characterization of the binding and, in particular, its stoichiometry, was accomplished via quartz crystal microgravimetry. Here, a film of **1** was prepared on a metal-coated crystal surface and exposed to guest molecules in the vapor phase. According to the Sauerbrey equation, mass uptake (Δm) at the piezoelectric quartz crystal and/or its coating, is characterized by a decrease in the crystal's fundamental frequency (f), where A_e is the electrode area [34] Fig. 1:

$$\Delta f = -(56.6 \text{ Hz cm}^2\ \mu\text{g}^{-1})\ \Delta m/A_e \quad (1)$$

Table 1
Absorption maximum (nm) of the Soret band for derivatized thin films of $[Re(CO)_3(Cl)(Zn\text{-}5,15\text{-}Py_2P)]_4$ in hexanes (unless noted otherwise) and comparison with the maximum shift observed in dichloromethane solution for a 50 ± 10 μM solution of $[Re(CO)_3(Cl)(Zn\text{-}5,15\text{-}Py_2P)]_4$ in the presence of excess ligand

Imine		pK_a[a]	Soret film (solution)	Q film (solution)	Q′ film (solution)
	None	418 (418)	546 (544)	580 (580)	
2	3,5-Dichloropyridine	0.67[b]	420 (426)	550 (550)	588 (582)
3	3,5-Dibromopyridine	0.82[b]	418 (426)	548 (550)	580 (584)
4	3,4-Dicyanopyridine		420 (422)	548 (548)	582 (580)
5	4-Cyanopyridine	1.86[b]	428 (426)	554 (552)	590 (584)
6	3-Bromopyridine	2.84	430 (426)	554 (550)	588 (584)
7	4-Acetylyridinek	3.51	430 (426)	554 (552)	588 (586)
8	4-Bromopyridine[k]	3.78	450	554	558
9	2,2′-Bipyridine	4.44[c]	418 (420)	546 (552)	580 (580)
10	2,4-Bipyridine	4.77[c]	434 (430)	556 (552)	590 (586)
11	4,4′-Bipyridine	4.82[c]	434 (428)	556 (554)	590 (586)
12	4,4′-Trimethylenebipyridine		434 (430)	556 (554)	590 (586)
13	1,2-Bis(4-pyridyl)ethane		434 (430)	556 (554)	590 (588)
14	1,2-Bis(4-pyridyl)ethylene	5.6[d]	434 (430)	556 (552)	590 (556)
15	Pyridine	5.21[b]	432 (429)	556 (552)	590 (556)
16	4-Phenylpyridine	5.55	432 (430)	556 (552)	590 (556)
17	4-′Bu-pyridine	5.99	432 (432)	556 (554)	588 (558)
18	4-Picoline	6.03[b]	432 (430)	556 (554)	590 (588)
19	3,5-Lutidine	6.14[b]	430 (430)	556 (554)	592 (586)
20	3,4-Lutidine	6.48[b]	432 (430)	556 (554)	592 (588)
21	2,6-Lutidine	6.62[c]	418 (422)	550 (548)	592 (578)
22	*Trans*-3-Pyrrol-1-yl-methylpyridine		432 (428)	556 (552)	592 (586)
23	4-Pyrolidinopyridine		434 (430)	558 (556)	592 (590)
24	4-Aminopyridine	9.17	434 (430)	558 (554)	592 (588)
25	4-(*N*,*N*-Dimethylamino) pyridine	9.71	434 (430)	558 (556)	592 (588)
26	*Trans*-3-(3-Pyridine) acrilic acid[k]		418 (426)	546 (550)	580 (584)
27	3-Pyridinesulfonic acid[k]	3.22	420	546	580
28	3,5-Pyridine-dicarboxylic acid[k]	3.57[f]	422	548–550	592
29	Isonicotinamide[k]	3.61[g]	422 (428)	548 (552)	582 (586)
30	Isonicotinic acid[k]	4.86	422	550	586
31	Nicotinic acid[k]	4.81	422	548–550	592
32	Picolinic acid[k]	5.32	420 (418)	546 (554)	582 (578)
33	Benzimidazole	5.53	420 (430)	550 (554)	582 (582)
34	Imidazole	7.00	432 (430)	558 (556)	588 (586)
35	1-Vinylimidazole		434 (430)	558 (556)	592 (586)
36	1-Methylimidazole	7.30	436 (430)	558 (556)	592 (588)
37	Quinoxaline	0.56	418 (422)	548 (546)	580–582 (580)
38	Phenazine	1.2	418 (interference)	546 (544)	580 (580)
39	Pyrazine	0.65	424 (426)	550-552 (550)	584–588 (586)

Table 1 (continued)

Imine		pK_a[a]	Soret film (solution)	solu-Q film (solution)	Q' film (solution)
40	Pyrimidine	1.31	434 (426)	556 (550)	590 (586)
41	Pyrazole	2.52	432 (428)	554 (552)	588–592 (584)
42	1,4-(4-Ethylpyridyl) benzene[h]		----(426)		
43	H_2-5,15-Py_2P[h,i]		----(426)		
44	H_2-Py_4P[h,j]		----(426)		

[a] From Refs. [21–24], unless noted otherwise.
[b] Ref. [25].
[c] Ref. [26].
[d] Ref. [27].
[e] Ref. [31].
[f] Ref. [30].
[g] Ref. [29].
[h] Ref. [2].
[i] H_2-5,15-Py_2P = 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-(4-pyridyl)H_2-porphyrin).
[j] H_2-Py_4P = 5,10,15,20-tetrakis(4-pyridyl)H_2-porphyrin.
[k] Value obtained in water.

3.3. Stability and ligand release studies

The stability of host/guest complexes was studied in the vapor phase with a representative set of ligands (pyrazine, 4-cyanopyridine, 3-bromopyridine, pyridine and 4-picoline) over a period of 20 h. Ligation initially caused a 8–12 nm red shift

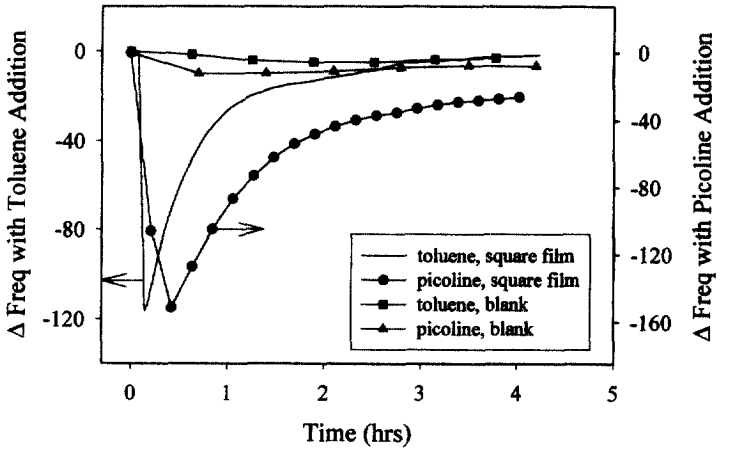


Fig. 1. Comparative QCM responses from a thin film of **1** indicating coordination of 4-picoline (circles), but only weak, nonspecific binding of toluene (no symbol).

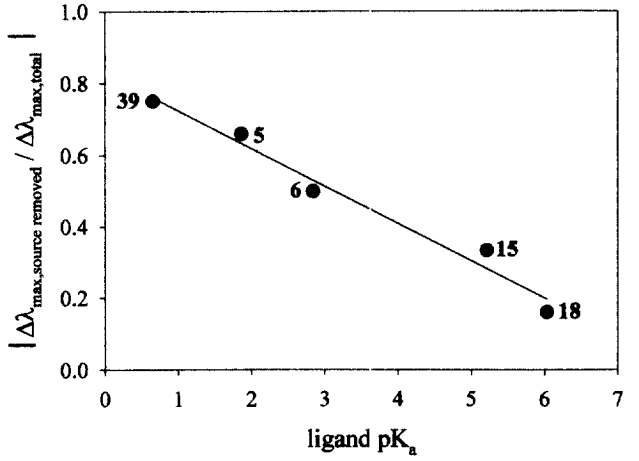


Fig. 2. Ratio of the displacement of the Soret band remaining after 20 h of ligand release (in air) for films of **1**, to the total displacement in a saturated atmosphere of the ligand (30 min). See Table 1 for numerical key to ligands.

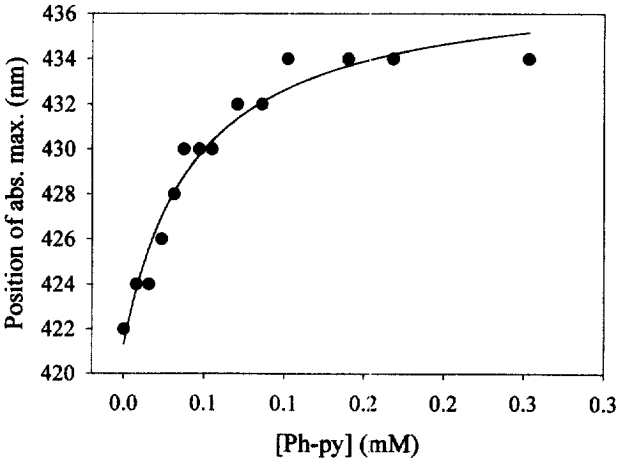


Fig. 3. Position of the Soret band for a film of **1**, with increasing concentration of 4-phenylpyridine in water. Additions of the guest were done as a concentrated acetone solution. Each spectrum was recorded 2 min after guest addition.

of the Soret band. Guest release was observed as a shift toward the original value. (With the resolution available, the two absorption bands expected for a mixture of bound and unbound Zn-porphyrin species were not resolved; only a broadening and shift of the absorption were observed.) Fig. 2 shows that the kinetic stability of the host/guest complex is dependent on the σ-donating ability of the guest. For example, the position of the Soret band, 20 h after exposure to the poorly

σ-donating pyrazine ligand, returns 75% of the way back its original value, while a film modified with 4-picoline ($pK_a = 6.03$) shifts back by only 16%.

Ligand release was also investigated in condensed phase (water, hexane) for the list of N-donors in Table 1. Ligand release (into solution) is highly dependent on the nature of the guest (hydrophobic nature, pK_a), and the solvent to which the film is exposed following the uptake of guest. For example, for a series of pyridines that show film uptake from hexane, the less basic guests (pyridine, 4-picoline, and 4-phenylpyridine; pK_a ca. 5–6) all leach from the films during overnight exposure to hexane, while films derivatized with 4-aminopyridine and 4-*N*,*N*-dimethylaminopyridine ($pK_a > 9$) show no evidence of ligand loss over the same period of time. However, even though derivatizations appear permanent in hexane, 4-*N*,*N*-dimethylaminopyridine and 4-aminopyridine are released in water. No appreciable release is observed, following overnight exposure to hexane, for **9**, **10**, **12**–**14**, **21**–**23**, **25**, **34**–**36** and **40**, while derivatization appears to be permanent in water (at least for 12 h), for **12**, **13**, **16**, **22**, **23** and **40**, among others. More quantitative ligand release studies were done, in water, for a few pyridines, and will be discussed in more detail in Section 3.4.

3.4. Quantitative binding studies

In order to place the binding on a more quantitative footing, and to assess the effect of solvophobic partitioning on guest uptake, binding constants (K_b) were determined for film-based uptake of several pyridines from water. Fitting of variable guest concentration data, illustrated in Fig. 3 for 4-phenylpyridine gave the apparent binding constants listed in Table 2. The data were fitted to the following expression, where λ_i is the position of the absorption maximum for variable guest concentrations, λ_0 is the absorption maximum in the absence of a guest molecule, $\Delta\lambda$ is the total shift in the absorption maximum over the course of the experiment, and $[L]$ is the concentration of guest.

$$\lambda_i = \lambda_0 + (K_b \times [L] \times \Delta\lambda)/(1 + (K_b \times [L])) \quad (2)$$

Binding constants for Zn-tetraphenylporphyrin (Zn-TPP) with N-donor ligands are available in solution, in benzene [35], toluene [36], and dichloromethane [37]. For most of the pyridines for which comparison with solution data is possible, the binding constants determined in thin films of **1** are of the same order of magnitude as for Zn-TPP in solution, indicating that the film offers an environment which approximates that of a non-ligating organic solvent. In the case of 4-aminopyridine, the K_b value determined in the film studies is markedly lower than that expected from the binding constants for Zn-TPP in dichloromethane.

The difference is attributed to the high hydrophilicity of this pyridine, which presumably favorably partitions into the aqueous phase (see below). (Note that the competitive protonation reaction of the amino group or the pyridinic nitrogen alone cannot account for the marked decrease in K_b compared to pyridines of similar pK_a values, since the K_b value obtained in pH 10 buffer is the same as that in unbuffered water.)

Table 2
Binding constants for various pyridines thin films of **1** (aqueous medium), and for Zn-tetraphenylporphyrin (Zn-Py_4P) in non-bonding solvents

		PK_a[a]	K_b (**1**) (film)	log K_b (**1**) (film)	log K_b (Zn-Py_4P) (solution)	log P[e]	$t_{1/2}$ (s)
5	4-Cyanopyridine	1.86	$(6.3 \pm 2.8) \times 10^2$	2.80	3.00[b]	0.46	~80
6	3-Bromopyridine	2.84	$(4.6 \pm 1.2) \times 10^3$	3.66	3.14[b]	1.33	$\sim 5.2 \times 10^2$
7	4-Acetylpyridine	3.51	$(9.6 \pm 2.0) \times 10^2$	2.98	3.51[b]	0.48	$\sim 1.9 \times 10^2$
8	4-Bromopyridine	3.78	$(7.7 \pm 1.4) \times 10^3$	3.89		1.58	$\sim 4.1 \times 10^2$
15	Pyridine	5.21	$(4.5 \pm 0.9) \times 10^3$	3.65	3.82[b] 3.78[c,d]	0.65	$\sim 1.8 \times 10^2$
16	4-Phenylpyridine	5.55	$(2.3 \pm 0.7) \times 10^4$	4.36		2.45	
18	4-Picoline	6.03	$(2.6 \pm 1.1) \times 10^3$	3.41	3.96[b] 4.02[c]	1.22	$\sim 2.6 \times 10^2$
24	4-Aminopyridine	9.17	$(1.9 \pm 0.4) \times 10^2$	2.28	4.49[b] 4.65[c]	0.27	$\sim 2.5 \times 10^2$
25	4-(*N*,*N*-Dimethyl-aminopyridine)	9.71	$(1.7 \pm 0.6) \times 10^4$	4.23	4.84[b]	1.16[f]	$\sim 3.4 \times 10^4$

[a] See Ref. in Table 1.
[b] In dichloromethane, Ref. [36].
[c] In benzene, Ref. [34].
[d] In toluene, Ref. [35]
[e] P is the octanol/water partition coefficient taken from Ref. [40].
[f] Estimated from a correlation between experimental log (P) values for pyridine and benzene derivatives [31].

In order to allow comparison of the film binding constants with those for a Zn-por7phyrin in water, binding constants were determined for a (cationic) water soluble porphyrin, Zn-*meso*-tetra(4-*N*-methyl-pyridyl)-porphyrin. Absorbance data, fitted to a binding expression analogous to Ú, yielded K_b values of 11.8 ± 1.1 M^{-1} and $1.3 \pm 0.1 \times 10^3$ M^{-1} for 4-picoline and 4-phenylpyridine, respectively. (Spectrofluorometry yielded 8.0 ± 0.5 M^{-1} for 4-picoline.) By comparing the Zn-*meso*-tetra-(4-*N*-methyl-pyridyl)-porphyrin) binding constants for these two pyridines in water to those for thin films of **1**, we infer that hydrophobic partitioning into the film increases K_b for the latter by ca. two orders of magnitude.

For zinc porphyrins in nonaqueous solution, the log of the binding constant is expected to scale roughly with the pK_a of the ligand [32,34,36,38–40]. Fig. 4 shows the dependance of $\log(K_b)$ (thin films of **1** in water) on ligand pK_a. For the series of pyridines represented with filled circles we observe the expected linear relation. However, three hydrophobic pyridines, represented by open circles, have binding constants higher than expected based on the ligand's electron-donating properties alone. If only the moderately hydrophilic pyridines, represented in Fig. 4 by filled symbols, are fitted to Eq. (3), an intercept (α) of 2.5 and a slope (β) of 0.19 are obtained. For comparison, plots of $\log(K_b)$ versus ligand (pyridine) pK_a for Zn-TPP in solution yielded slopes of 0.24 in both benzene [34] and dichloromethane [36].

$$\log(K_b) = \alpha + \beta\ (pK_a) \tag{3}$$

A better fit of the available film binding data, including the more hydrophobic imines, was obtained by taking into account ligand hydrophobic effects. As

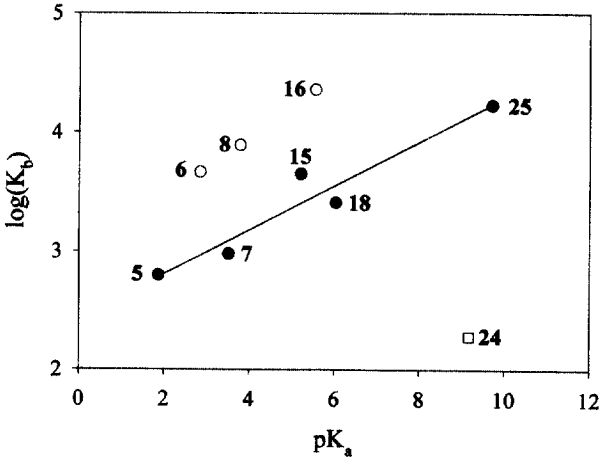


Fig. 4. Dependance of film-based binding constants on ligand pK_a. For a series of pyridines of comparable hydrophilicity (●), a linear correlation between the pK_a of the ligand and $\log(K_b)$ is observed. More hydrophobic pyridines (○) show higher binding than predicted from ligand basicity, while the binding constant for 4-aminopyridine (□) is unusually low. (See Table 2 for ligand numbering; Only **5**, **7**, **15**, **18** and **25** are included in the regression.)

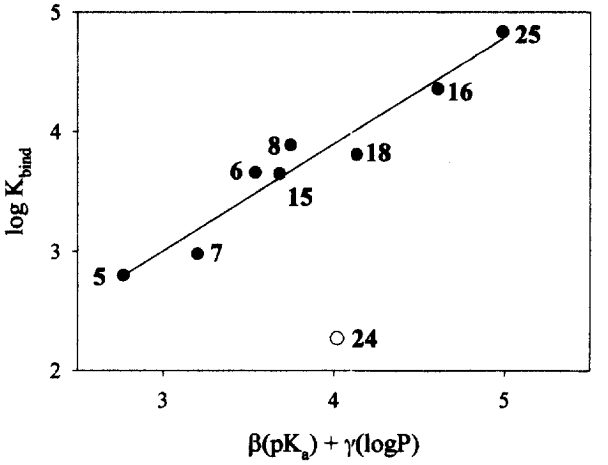


Fig. 5. Relation between the observed binding constant, the ligand pK_a, and the relative ligand hydrophobicity for the series of pyridines investigated. (See Table 2 for ligand numbering scheme.)

estimates for relative hydrophobicity, we utilized previously measured water → octanol partition coefficients, P [41]. The results of a combined fit (Eq. (4)) are shown in Fig. 5

$$\log(K_b) = \alpha + \beta\ (pK_a) + \gamma\ \log(P) \tag{4}$$

From the fit, β is 0.24, α is 2.1, γ is 0.48, and the correlation coefficient, r is 0.973. While the correlation is sufficiently strong to suggest predictive utility, it should be noted that the relationship breaks down for 4-aminopyridine (not included in the fit)—the only pyridine on the plot which has a hydrogen bond donating substituent. A potential secondary correlation between K_b, pK_a and P for pyridines bearing hydroxyl or amino substituents could not be investigated since none of these moderately basic ligands showed appreciable binding in water (see Table 1, molecules **26–32**).

Predictions concerning the kinetic stability of the host/guest assembly (upon removal of the source of ligand) can also be made: we find that the half life for the film-based metal/ligand assembly in water (Table 2) roughly follows the binding constant. Note that the 4-phenylpyridine system shows no detectable ligand loss after 24 h in water, while only slow ligand release is encountered for 4-*N*,*N*-dimethylaminopyridine, consistent with the unusually large thermodynamic binding constants for these species. In other cases, however, ligand release occurs in as little as 80–200 s. Finally, note that in comparison with the vapor-phase ligand release described in Section 3.3, immersion of the film-based assembly in water generally accelerates the release kinetics. The acceleration presumably reflects both incipient product stabilization due to ligand solvatation and incipient stabilization due to Zn(II)–water coordination.

Despite the explanations for relative kinetic stability, a question remains concerning the origin of the exceptionally large absolute kinetic stabilities in thin-film environments; Zn(II)–porphyrin ligation is generally much less persistent in solution environments. One possible explanation concerns the kinetics of the corresponding ligand attachment reaction. If this process is so rapid that it is diffusion limited, then the thermodynamic binding constant can be written as:

$$K_b = \text{binding rate constant/release rate constant} = k_{diffusion}/k_{release} \times [\text{ligand}] \quad (5)$$

For related mesoporous films, we have recently observed that diffusion coefficients for several molecular probe species are considerably smaller within the film than in solution [10]—even prior to correction of the former for likely favorable partitioning effects. If one further recognizes that diffusion in solution is a highly efficient three-dimentional process, but that film-based diffusion likely occurs by a much more restrictive (much less efficient) quasi-1D process, then for a constant K_b value, $k_{release}$ must be much smaller in the film environment (and $t_{1/2}$ (release) must be much larger).

4. Conclusion

Molecular materials based on thin films of the zinc-containing tetraporphyrinic square assembly, **1**, can be rapidly and, in many cases, completely functionalized by exposure to aqueous or alkane solutions of good N-donor ligands such as pyridine and imidazole. Modification can also be achieved via direct vapor-phase exposure of films to volatile ligands. In both experiments, modification is a consequence of simple Zn(II) coordination chemistry and is facilitated by the exceptional mesoporosity of the parent material. Vapor-phase quartz crystal microbalance experiments indicated an average ligand/component square binding stoichiometry of 2.5, in fair agreement with the stoichiometry of **4** implied by absorbance measurements and expected from the number of Zn(II) sites per assembly. Systematic studies with **9** of the more than 40 total ligands examined, show that ligand binding strength is controlled by both ligand basicity (σ electron donating ability) and ligand solvophobic phenomena. In several instances, the film modification chemistry was found to be reasonably persistant; in a few instances the modification was demonstrably permanent. For modified mesoporous films in contact with liquid environment, kinetic stability could be qualitatively correlated with thermodynamic stability, as indicated by binding constants. Kinetic stability under these conditions, therefore, is a function of both ligand–N/Zn(II) bond strength and ligand solvophobic character. For films in contact with an inert atmosphere (air), kinetic stability could be correlated successfully with simply the ligand–N/Zn(II) bond strength (as inferred from the ligand pK_a). The combined results support the notion that mesopore derivatization—leading to systematic alteration of component cavity size, shape, and chemical affinity—can be usefully achieved via axial ligation of metalloporphyrins. We suggest that the ready availability of an extended array of

derivatized thin film materials could be useful in membrane-based transport applications, catalyst applications, and/or chemical sensing applications.

Acknowledgements

The authors thank R.V. Slone for preparing compound **1**. We thank the Office of Naval Research, the US Geological Survey (Illinois Water Resources Center), the National Oceanic and Atmospheric Administration and most recently, the NSF, for financial support. S. Bélanger thanks the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche for post-doctoral funding. J. Welch acknowledges the Northwestern Material Research Center (NSF-DMR-9632472) for providing a summer undergraduate research fellowship.

References

[1] R.V. Slone, J.T. Hupp, C.L. Stern, T.E. Albrecht-Schmitt, Inorg. Chem. 35 (1996) 4096.
[2] R.V. Slone, J.T. Hupp, Inorg. Chem. 36 (1997) 5422.
[3] M. Fujita, J. Yakazi, K. Ogura, J. Am. Chem. Soc. 112 (1990) 5645.
[4] M. Fujita, S. Nagao, M. Iida, K. Ogata, K. Ogura, J. Am. Chem. Soc. 115 (1993) 1574.
[5] M. Fujita, J. Yagazi, K. Ogura, Tetrahedron Lett. 32 (1991) 5589.
[6] R.V. Slone, D.I. Yoon, R.M. Calhoun, J.T. Hupp, J. Am. Chem. Soc. 117 (1995) 11813.
[7] P.A. Gale, Z. Chen, M.G.B. Drew, J.A. Heath, P.D. Beer, Polyhedron 17 (1998) 405.
[8] P.D. Beer, J. Chem. Soc. Chem. Commun. (1996) 689.
[9] K.D. Benkstein, J.T. Hupp, C.L. Stern, J. Am. Chem. Soc. 120 (1998) 12982.
[10] S. Bélanger, J.T. Hupp, C.L. Stern, R.V. Slone, D.F. Watson, T.M. Carrell, J. Am. Chem. Soc. 121 (1999) 557.
[11] R.V. Slone, K.D. Benkstein, S. Bélanger, J.T. Hupp, I.A. Guzei, A.L. Rheingold, Coord. Chem. Rev. 171 (1998) 221.
[12] P.J. Stang, D.H. Cao, S. Saito, A.M. Arif, J. Am. Chem. Soc. 117 (1995) 6273.
[13] P.J. Stang, K. Chen, A.M. Arif, J. Am. Chem. Soc. 119 (1997) 2524.
[14] J.A. Whiteford, C.V. Lu, P.J. Stang, J. Am. Chem. Soc. 119 (1997) 2524.
[15] S.G. Yan, J.T. Hupp, J. Electroanal. Chem. 397 (1995) 119.
[16] S. Bélanger, K.J. Stevenson, S.D. Mudakha, J.T. Hupp, Langmuir 15 (1999) 837.
[17] S. Bélanger, J.T. Hupp, Angew. Chem. Int. Ed. Engl. (1999) in press.
[18] M.D. Ward, D.A. Buttry, Science 240 (1990) 1000.
[19] R. Schmacher, Angew. Chem. Int. Ed. Engl. 29 (1990) 329.
[20] L.A. Lyon, J.T. Hupp, J. Phys. Chem. 99 (1995) 15718.
[21] D.G. Whitten, I.G. Lopp, P.D. Wildes, J. Am. Chem. Soc. 90 (1968) 7196.
[22] E.F.V. Scriven, in: A.R. Katritzky, C.V. Rees (Eds.), Comprehensive Heterocyclic Chemistry, Pergamon Press, NY, 1984, Part 2 A, p. 171.
[23] D.J. Brown, in: A.R. Katritzky, C.V. Rees (Eds.), Comprehensive Heterocyclic Chemistry, Pergamon Press, NY, 1984, Part 2 B, p. 60.
[24] A.E.A Porter, in: A.R. Katritzky, C.V. Rees (Eds.), Comprehensive Heterocyclic Chemistry, Pergamon Press, NY, 1984, Part 2 B, p.162.
[25] A.R. Katritzky, J.M. Cagowski, in: A.R. Katritzky, C.V. Rees (Eds.), Comprehensive Heterocyclic Chemistry, Pergamon Press, NY, 1984, Part 4 A, p. 384.
[26] A. Fischer, W.J. Galloway, J. Vaughan, J. Chem. Soc. (1964) 3591.
[27] P. Krumholz, J. Am. Chem. Soc. 73 (1951) 3487.

[28] G. Beggiato, G. Favaro, U. Mazzucato, J. Heterocycl. Chem. 7 (1970) 583.
[29] J. Ulstrup, J. Chem. Soc. Faraday Trans. I 71 (1975) 435.
[30] H.H.G. Jellinek, J.R. Urwin, J. Phys. Chem. 58 (1954) 548.
[31] J.C. Lewis, J. Biol. Chem. 247 (1972) 1861.
[32] K. Schofield, Heterto Aromatic Nitrogen Compounds, Plenum Press, NY, 1967, p. 168.
[33] K.M. Kadish, L.R. Shiue, Inorg. Chem. 21 (1982) 3623.
[34] G.Z. Sauerbrey, Physica 155 (1959) 206.
[35] C.H. Kirksey, P. Hambright, C.B. Storm, Inorg. Chem. 8 (1969) 2141.
[36] P. Bhyrappa, V. Krishnan, M. Nethaji, J. Chem. Soc. Dalton Trans. (1993) 1901.
[37] K.M. Kadish, L.R. Shiue, R.K. Rhodes, L.A. Bottomley, Inorg. Chem. 20 (1981) 1274.
[38] C.H. Kirksey, P. Hambright, Inorg. Chem. 9 (1970) 958.
[39] K.M. Kadish, L.R. Shiue, Inorg. Chem. 21 (1982) 1112.
[40] K.M. Kadish, D.J. Leggett, D. Chang, Inorg. Chem. 21 (1982) 3618.
[41] F. Gago, J. Alvarez-Builla, J. Elguiro, J. Chromatogr. 449 (1988) 95.