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Tetra(*N*-*R*-pyridinium-4-yl)porphyrin and tetra(*N*-*R*-pyridinium-3-yl)porphyrin derivatives were synthesized with *R* = 3, 6, and 8 carbon alkene, alcohol and carboxylic acid chains. Self-aggregation of these systems was studied at *I* = 0.1 using visible spectroscopy. *N*-Alkyl chain length and functionality were determined to play the dominant role in aggregation of the cationic porphyrins. Position of peripheral charge (*meta* vs. *para*) also influenced spectral changes and the nature of the aggregate.

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Introduction.

Self-assembly of porphyrin supramolecular systems is of interest in the development of nanomolecular devices, light harvesting arrays, oxygen transport systems and DNA structure probes [1-4]. Understanding factors that influence porphyrin self-organization is essential to designing and controlling supramolecular systems. Association of porphyrins through π - π stacking to form dimers and higher aggregates is well established [5]. Several cationic systems such as tetra-(*N,N,N*-trimethylanilinium-4-yl)porphyrin and trans-di(*N*-methylpyridinium-4-yl)diphenylporphyrin aggregate in the presence of inorganic salts [6-8]. In contrast, tetra(*N*-methylpyridinium-4-yl)porphyrin has been extensively studied

and does not appear to self-aggregate even upon increasing ionic strength [9-11]. To systematically determine the influence of *N*-alkyl chain length, *N*-alkyl chain functionality, and peripheral charge distribution (*meta* vs. *para*) on cationic porphyrin self-association, we synthesized a series of cationic pyridiniumylporphyrins (Figure 1) and studied aggregation in these systems.

Aggregation Studies.

A typical visible absorbance spectrum for a porphyrin consists of an intense Soret band (B band) and four Q bands. The Soret band is particularly sensitive to porphyrin-porphyrin interactions. Hypochromicity, shifting and broadening of the Soret band have been observed as indicators of

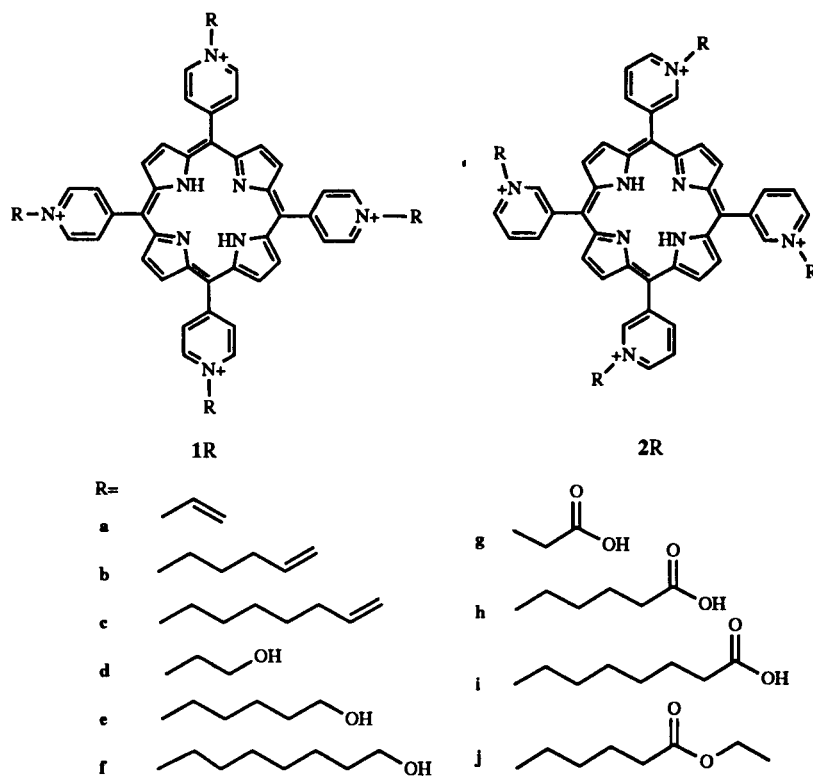


Figure 1. Cationic porphyrins 1a-j and 2a-j.

Table 1
Aggregation Concentrations [a]

Porphyrin	Aggregation Concentration	Porphyrin	Aggregation Concentration
1a	$2 \times 10^{-5} M$	2a	$5 \times 10^{-6} M$
1b	$5 \times 10^{-6} M$	2b	$1 \times 10^{-6} M$
1c	$1 \times 10^{-6} M$	2c	$1 \times 10^{-6} M$
1d	$1 \times 10^{-5} M$	2d	$5 \times 10^{-6} M$
1e	$5 \times 10^{-6} M$	2e	$1 \times 10^{-6} M$
1f	$1 \times 10^{-6} M$	2f	$1 \times 10^{-6} M$
1g [b]	aggregation not observed	2g [b]	aggregation not observed
1h [b]	aggregation not observed	2h [b]	aggregation not observed
1h	$5 \times 10^{-5} M$	2h	$3 \times 10^{-5} M$
1i [b]	aggregation not observed	2i [b]	aggregation not observed
1i	$5 \times 10^{-5} M$	2i	$1 \times 10^{-5} M$
1j	$5 \times 10^{-5} M$	2j	$2 \times 10^{-5} M$

[a] Concentration at which hypochromicity was observed. [b] pH 9.0.

porphyrin association [7-9, 12-17]. Cationic pyridiniumyl-porphyrins with long alkyl chains (octyl, dodecyl and octadecyl) have been shown to form micelles exemplified by red shifts and decreased Soret band extinction coefficients [12,13]. Micellar porphyrin fibers and vesicles have been reported with broadened, split Soret bands [12]. Increasing ionic strength induces aggregation of tetra(*N,N,N*-trimethylanilinium-4-yl)porphyrin and trans-di(*N*-methylpyridinium-4-yl)diphenyl porphyrin which is accompanied by a slight red shift (1-2 nm) and broadening of the Soret band [7,8]. Changes in the Soret band have also been used to quantify association of nucleotides and other small molecules with porphyrins through π - π interactions [9,14,17]. Hypochromicity, shifts and broadening of the Soret band are used in this study to evaluate aggregation.

In water, the Soret band for 1a-j appeared at 424 nm (extinction coefficients appear in experimental) and the Q bands at 519, 556, 585, and 641 nm. For 2a-j, the Soret band appeared at 418 nm with Q bands at 514, 550, 581, 636 nm. Similar spectra have been reported for tetra(*N*-methylpyridinium-4-yl)porphyrin, tetra(*N*-methylpyridinium-3-yl)porphyrin and other alkylated pyridyl-porphyrins [12,13].

Over the concentration range $1 \times 10^{-7} - 1 \times 10^{-4} M$ (ionic strength approximately zero), all of the porphyrin systems 1a-j and 2a-j obeyed Beer's Law. Carboxylic acid systems 1g-i and 2g-i did not deviate from Beer's Law even upon the addition of 1 mM Tris (pH 8.5-9.0). No evidence for self-aggregation was observed in the visible spectra of these systems.

The addition of 0.1 M potassium nitrate promoted aggregation. Concentrations at which hypochromicity was initially observed are listed in Table 2. Only 1i-j and 2i-j at pH 9.0 were unaffected by the addition of salt. Visible spectra of tetra(*N*-R-pyridinium-4-yl)porphyrin (R = allyl, hexenyl and octenyl, 1a-c) are shown in Figure 2. As the alkene chain length increased, the extent of higher aggregation increased as indicated primarily by the reduction in Soret band intensity. Q Bands (500-700 nm) changed only slightly with a small bathochromic shifts and broadening. Beer's Law plots at 424 nm (Figure 3) for the 1a-c systems demonstrated deviation from linearity further indicating aggregate formation.

To characterize the extent of self-association [16], the percent hypochromicity ($(\epsilon_1 = 0 - \epsilon_1 = 0.1 / \epsilon_1 = 0) \times 100$), band broadening (change in width at half-height, $\Delta w_{1/2}$) and wavelength shifts of the Soret bands were compiled (Table 2). As *N*-alkyl chain length increased and polarity of the *N*-alkyl functionality decreased (alkene > OH > COOH), Soret band hypochromicity and half-width

Table 2
Soret Band Spectral Changes

Porphyrin	$\Delta\lambda$	% H [a]	% H [b]	$\Delta w_{1/2}$ [a]	$\Delta w_{1/2}$ [b]	Porphyrin	$\Delta\lambda$	% H [a]	% H [b]	$\Delta w_{1/2}$ [a]	$\Delta w_{1/2}$ [b]
1a	2 nm	0	6	1 nm	3 nm	2a	1 nm	3	11	1 nm	4 nm
1b [d]	2	8	24	2	2	2b [d]	1	13	20	2	3
1c [d]	6	56	76	26	43	2c [d]	1	33	57	0	4
						2c [c,d]	1	18	58	1	5
1d	1	4	4	2	2	2d	1	5	9	1	2
1e	1	9	16	2	4	2e	1	18	23	3	4
1f [d]	2	26	75	5	39	2f [d]	2	13	32	2	4
						2f [c,d]	1	10	26	1	3
1g [c]	1	0	0	0	1	2g [c]	1	3	0	0	0
1h [c]	1	0	2	2	3	2h [c]	1	2	2	0	0
1h	2	0	7	0	1	2h	1	0	5	2	3
1i [c]	2	2	4	0	2	2i [c]	1	1	1	0	3
1i [d]	2	0	23	2	3	2i [d]	1	5	11	1	1
1j [d]	2	0	87	2	12	2j	1	2	6	0	2

[a] $1 \times 10^{-5} M$, %H = $(\epsilon_1 = 0 - \epsilon_1 = 0.1 / \epsilon_1 = 0) \times 100$. [b] $1 \times 10^{-4} M$, %H = $(\epsilon_1 = 0 - \epsilon_1 = 0.1 / \epsilon_1 = 0) \times 100$. [c] pH 9.0. [d] precipitate formed at concentrations $> 10^{-4} M$.

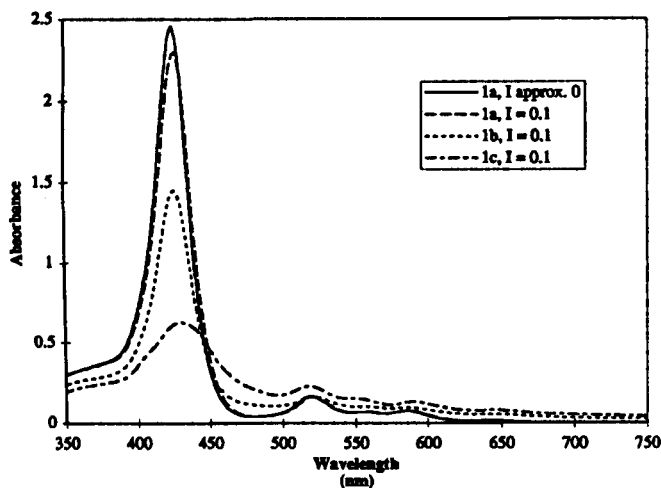


Figure 2. Visible spectra of tetra(*N*-*R*-pyridinium-4-yl)porphyrins (*R* = allyl (**1a**), hexenyl (**1b**), octenyl (**1c**)) in water (0.1 cm path length).

increased. Small bathochromic shifts were observed for all systems; with a maximum shift of +6 nm recorded for **1c**. Only carboxylic acids **1i-j** and **2i-j** exhibited pH dependent spectral variations.

Generally, the spectroscopic changes correspond to an aggregation model proposed for similar porphyrin systems [17,18]: monomers, dimers and lower aggregates form micelles, higher aggregates and precipitates as porphyrin concentration increases.

For porphyrins with long alkyl chains **1c,f,j** and **2c,f**, the sharp decreases in Soret band extinction coefficients and broadening indicated micelle formation [12,13,18]. The concentrations listed in Table 1 should be considered critical micelle concentrations for **1c,f,j** and **2c,f**.

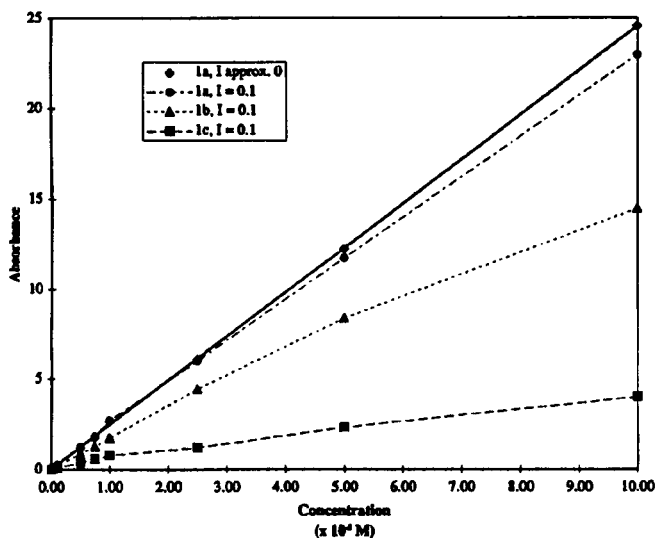


Figure 3. Soret band Beer's Law plots for tetra(*N*-*R*-pyridinium-4-yl)porphyrins (*R* = allyl (**1a**), hexenyl (**1b**), octenyl (**1c**)) at 424 nm.

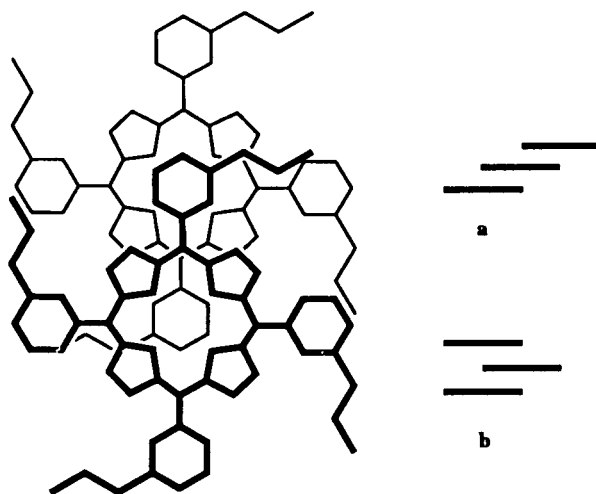


Figure 4. Proposed pre-micellar aggregate for cationic 3-pyridyl derivatives **2a-j**: (a) staircase and (b) staggered arrangements are possible.

Decreasing alkyl chain length and increasing polarity typically result in higher critical micelle concentration [19]. Over the concentration range studied, most three carbon and six carbon chain systems were forming lower order, pre-micellar aggregates.

Only small shifts in the Soret band were observed for **1a-j** and **2a-j**. Aggregation of other porphyrin systems has been reported with no Soret band shifts [18]. Slight shifts were also reported for other cationic porphyrins at high ionic strength [7,8].

Location of the positive charge on the porphyrin periphery (*meta* vs. *para*) affected spectral changes associated with aggregation. The 3-pyridyl derivatives aggregated at lower concentrations (Table 1) and showed slightly more hypochromicity at lower concentrations than 4-pyridyl systems (Table 2). The apparent increased tendency of the 3-pyridyl systems to aggregate may be explained by considering resonance stabilization of the pyridinium cation. For the 4-pyridyl systems, the positive charge is delocalized over the porphyrin π system [20,21]. However, in the 3-pyridyl position, the positive charge is localized on the pyridine ring. Tetra(*N*-methylpyridinium-3-yl)porphyrin is approximately 2.5 times as basic as tetra(*N*-methylpyridinium-4-yl)porphyrin [21]. The electron-rich 3-pyridyl core should readily form π - π stacking aggregates with the pyridinium cation (Figure 4). A staircase or staggered aggregate formed by the association of the positive pyridine ring and a neighboring electron-rich porphyrin core is a likely configuration for aggregates of **2**. Staircase stacking for similar π - π systems has been predicted [15]. The spectral changes observed in this study are consistent with pyridinium-porphyrin interactions [17] rather than porphyrin π - π coupling. Low hypochromicity and broadening of the 4-pyridyl systems

indicated minimal formation of premicellar aggregates consistent with lack of aggregation for tetra(*N*-methylpyridinium-4-yl)porphyrin [9-11].

Spectroscopic results for ester and carboxylic acid derivatives were not consistent with the overall aggregation trends already presented. Only slight spectral changes in the Soret band were observed for ester **2j** while **1j** displayed dramatic micelle formation (%H = 87). Upon increasing ionic strength (> 1.0 *M* potassium nitrate) for **2j**, micelle formation and precipitation occurred. For ionic surfactants, critical micelle concentration typically decreases as ionic strength is increased [19]. Ester system **2j** appeared to have an unusually high critical micelle concentration.

At pH 9, no deviation from Beer's Law or significant hypochromicity was observed for **1i-j** and **2i-j**. Ion-pairing of the carboxylate anions and the pyridinium cation would be expected particularly at high pH. The alignment of carboxylate and pyridinium groups of neighboring porphyrins would position the porphyrin centers a large distance apart and spectral changes indicating such aggregation would not occur. Consequently, the lack of band shift does not preclude formation of an ion-paired dimer.

In conclusion, addition of inorganic salt induced aggregation in the cationic systems studied. *N*-Alkyl chain length and functionality played the dominant role in aggregation of **1** and **2** cationic porphyrins. Position of peripheral charge influenced spectral changes and the nature of the aggregate.

Porphyrin systems which self-aggregate exhibit a unique DNA binding mode [8]. Tetra(*N*-methylpyridinium-4-yl)porphyrin has been shown to intercalate into DNA while self-aggregating cationic porphyrins bind in the minor groove of DNA with self-stacking generating a helical porphyrin assembly along the DNA template [7,8]. Using the results of these aggregation studies, we are presently exploring DNA-porphyrin interaction with **1a-j** and **2a-j**.

EXPERIMENTAL

A Shimadzu 3101 UV-Vis-NIR spectrophotometer was used to obtain electronic spectra. The IR spectra were recorded on a Nicolet 510P FTIR spectrophotometer as potassium bromide pellets. The NMR spectra were obtained with a JEOL GSX 400 MHz NMR spectrometer. Chemical shifts were measured in parts per million (ppm) relative to solvent isotopic impurity. Elemental analyses were performed by Microanalytical Laboratory, University of California, Berkeley, California and Atlantic Microlabs, Norcross, Georgia.

All reagents were reagent grade and used as received unless otherwise noted. Anhydrous DMF was purchased from Aldrich. 5,10,15,20-tetra(4-pyridyl)porphyrin and 5,10,15,20-tetra(3-pyridyl)porphyrin were obtained from Midcentury Chemicals

and used without additional purification. Alkylating agents were purchased from Aldrich. Bromoalkenes and bromoalcohols were purified by vacuum distillation. Bromocarboxylic acids were recrystallized. All alkylated porphyrins were isolated by size exclusion chromatography with lipophilic Sephadex (LH-20, Sigma) using methanol as the eluent.

Aggregation Studies.

Electronic spectra were obtained for $1.0 \times 10^{-7} M$ – $4.0 \times 10^{-4} M$ porphyrin solutions using 0.1 cm and 1 cm cuvettes. Aggregation was induced by addition of potassium nitrate (0.1 *M*). Higher pH solutions (pH 9.0) were prepared by the addition of 1 mM tris(hydroxymethyl)aminomethane. Nanopure water was used in all studies. Beer's law experiments were performed at room temperature.

General Alkylation Procedure for 5,10,15,20-Tetra(4-pyridyl)porphyrins (**1a-j**).

5,10,15,20-Tetra(4-pyridyl)porphyrin (30 mg, 0.05 mmole) was warmed to 100° in anhydrous dimethylformamide under nitrogen. Alkylating agent (2 mmoles) was dissolved in anhydrous dimethylformamide and added slowly to the porphyrin solution. The mixture was refluxed for 4 hours and cooled to 0°. The resulting purple precipitate was recovered by vacuum filtration, washed with DMF/ether and dried. The tetraalkylated product was isolated using exhaustive size exclusion chromatography (1: 2 cm x 20 cm, 2: 1 cm x 40 cm).

5,10,15,20-Tetra(*N*-allylpyridinium-4-yl)porphyrin (**1a**).

Alkylation with allyl bromide produced **1a** in 43% yield as a purple solid; ¹H nmr (dimethyl sulfoxide-*d*₆): δ 9.54 (d, 8H, py, *J* = 6.7 Hz), 9.25 (s, 8H, β-pyrrole), 9.05 (d, 8H, py, *J* = 6.7 Hz), 6.05 (m, 4H, H₂), 5.84, 5.72 (dd, 8H, H₃, H₃, *J* = 17.1, 10.0 Hz), 5.67 (t, 8H, H₁, *J* = 6.1 Hz), -3.09 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/(ε x 10⁴ M⁻¹ cm⁻¹) 424 (24.5), 519 (1.86), 556 (0.66), 585 (0.73), 641 (0.15).

Anal. Calcd. for C₅₂H₄₆N₈Br₄•6H₂O: C, 51.57; H, 4.83; N, 9.26. Found: C, 51.71; H, 4.51; N, 8.96.

5,10,15,20-Tetra(*N*-5-hexenylpyridinium-4-yl)porphyrin (**1b**).

Alkylation with 6-bromo-1-hexene produced **1b** in 79% yield as a purple solid; ¹H nmr (dimethyl sulfoxide-*d*₆): δ 9.61 (d, 8H, py, *J* = 6.6 Hz), 9.25 (s, 8H, β-pyrrole), 9.05 (d, 8H, py, *J* = 6.6 Hz), 6.00 (m, 4H, H₅), 5.20, 5.10 (dd, 8H, H₆, H₆, 17.0, 10.0 Hz), 5.00 (t, 8H, H₁, *J* = 6.1 Hz), 2.30 (m, 16H, H₂, H₄), 1.75 (m, 8H, H₃), -3.10 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/(ε x 10⁴ M⁻¹ cm⁻¹) 424 (23.7), 519 (1.60), 556 (0.72), 585 (0.72), 641 (0.21).

Anal. Calcd. for C₆₄H₇₀N₈Br₄•7H₂O: C, 55.00; H, 6.06; N, 8.02. Found: C, 54.70; H, 5.90; N, 7.70.

5,10,15,20-Tetra(*N*-7-octenylpyridinium-4-yl)porphyrin (**1c**).

Alkylation with 8-bromo-1-octene produced **1c** in 36% yield as a purple solid; ¹H nmr (dimethyl sulfoxide-*d*₆): δ 9.61 (d, 8H, py, *J* = 6.1 Hz), 9.25 (s, 8H, β-pyrrole), 9.04 (d, 8H, py, *J* = 6.1 Hz), 5.89 (m, 4H, H₇), 5.00 (m, 16H, H₈, H₈, H₁), 2.29 (m, 8H, H₂), 2.14 (m, 8H, H₆), 1.58 (m, 24H, H_{3,5}), -3.11 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/(ε x 10⁴ M⁻¹ cm⁻¹) 424 (23.1), 519 (1.54), 556 (0.62), 585 (0.67), 641 (0.17).

Anal. Calcd. for C₇₂H₇₆N₈Br₄•6H₂O: C, 58.37; H, 5.99; N, 7.57. Found: C, 58.03; H, 6.25; N, 7.63.

5,10,15,20-Tetra(*N*-3-hydroxypropylpyridinium-4-yl)porphyrin (**1d**).

Alkylation with 3-bromo-1-propanol produced **1d** in 62% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 9.60 (d, 8H, py, $J = 6.1$ Hz), 9.23 (s, 8H, β -pyrrole), 9.04 (d, 8H, py, $J = 6.1$ Hz), 5.06 (t, 8H, H_1 , $J = 6.1$ Hz), 5.01 (s, 4H, OH, deuterium oxide-exchangeable), 3.79 (m, 8H, H_3), 2.46 (m, 8H, H_2), -3.10 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 424 (26.5), 519 (1.73), 556 (0.76), 585 (0.93), 641 (0.26).

Anal. Calcd. for $\text{C}_{52}\text{H}_{54}\text{N}_8\text{O}_4\text{Br}_4 \cdot 7\text{H}_2\text{O}$: C, 47.99; H, 5.27; N, 8.62. Found: C, 47.94; H, 5.37; N, 8.21.

5,10,15,20-Tetra(*N*-6-hydroxyhexylpyridinium-4-yl)porphyrin (**1e**).

Alkylation with 6-bromo-1-hexanol produced **1e** in 72% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 9.60 (d, 8H, py, $J = 5.5$ Hz), 9.24 (s, 8H, β -pyrrole), 9.03 (d, 8H, py, $J = 5.5$ Hz), 4.92 (m, 8H, H_1), 4.49 (s, 4H, OH, deuterium oxide-exchangeable), 3.49 (br, 8H, H_6), 2.29 (m, 8H, H_2), 1.54 (m, 24H, H_{3-5}), -3.11 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 424 (23.5), 519 (1.57), 556 (0.63), 585 (0.68), 641 (0.16).

Anal. Calcd. for $\text{C}_{64}\text{H}_{78}\text{N}_8\text{O}_4\text{Br}_4 \cdot 5\text{H}_2\text{O}$: C, 53.64; H, 6.19; N, 7.82. Found: C, 53.75; H, 6.19; N, 7.38.

5,10,15,20-Tetra(*N*-8-hydroxyoctylpyridinium-4-yl)porphyrin (**1f**).

Alkylation with 8-bromo-1-octanol produced **1f** in 11% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 9.58 (d, 8H, py, $J = 5.5$ Hz), 9.25 (s, 8H, β -pyrrole), 9.04 (d, 8H, py, $J = 5.5$ Hz), 4.96 (m, 8H, H_1), 4.42 (s, 4H, OH, deuterium oxide-exchangeable), 3.43 (t, 8H, H_8 , $J = 7.0$ Hz), 2.29 (m, 8H, H_2), 1.47 (m, 40 H, H_{3-7}), -3.10 (s, 2H, internal NH) uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 424 (17.3), 519 (1.06), 556 (0.50), 585 (0.50), 641 (0.17).

Anal. Calcd. for $\text{C}_{72}\text{H}_{94}\text{N}_8\text{O}_4\text{Br}_4 \cdot 9\text{H}_2\text{O}$: C, 53.47; H, 6.98; N, 6.93. Found: C, 53.05; H, 6.50; N, 6.91.

5,10,15,20-Tetra(*N*-3-carboxyethylpyridinium-4-yl)porphyrin (**1g**).

Alkylation with 3-bromo-1-propionic acid produced **1g** in 18% yield as a purple solid; ^1H nmr (98% DMSO/2% deuterium oxide): δ 9.44 (d, 8H, py, $J = 6.1$ Hz), 9.20 (s, 8H, β -pyrrole), 8.91 (d, 8H, py, $J = 6.1$ Hz), 5.08 (t, 8H, H_1 , $J = 6.4$ Hz), 3.17 (t, 8H, H_2 , $J = 6.4$ Hz), -3.10 (s, 2H, internal NH); ir (potassium bromide): ν 1716.9 (C=O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 424 (20.0), 519 (1.40), 556 (0.58), 585 (0.65), 641 (0.16).

Anal. Calcd. for $\text{C}_{52}\text{H}_{46}\text{N}_8\text{O}_8\text{Br}_3$: C, 54.25; H, 4.03; N, 9.74. Found: C, 54.32; H, 4.40; N, 9.44.

5,10,15,20-Tetra(*N*-6-carboxypentylpyridinium-4-yl)porphyrin (**1h**).

Alkylation with 6-bromo-1-hexanoic acid produced **1h** in 34% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 9.61 (d, 8H, py, $J = 5.5$ Hz), 9.25 (s, 8H, β -pyrrole), 9.04 (d, 8H, py, $J = 6.1$ Hz), 4.98 (s, 8H, H_1), 2.37 (m, 8H, H_2), 2.36 (m, 8H, H_5), 1.73 (m, 8H, H_4), 1.61 (m, 8H, H_3), -3.10 (s, 2H, internal NH); ir (potassium bromide): ν 1716.9 (C=O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 424 (22.9), 519 (1.17), 556 (0.54), 585 (0.51), 641 (0.14).

Anal. Calcd. for $\text{C}_{64}\text{H}_{70}\text{N}_8\text{O}_8\text{Br}_4 \cdot 4\text{H}_2\text{O}$: C, 52.23; H, 5.34; N, 7.62. Found: C, 52.26; H, 5.15; N, 7.51.

5,10,15,20-Tetra(*N*-8-carboxyheptylpyridinium-4-yl)porphyrin (**1i**).

Alkylation with 8-bromo-1-octanoic acid produced **1i** in 47% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 9.59 (d, 8H, py, $J = 6.1$ Hz), 9.24 (s, 8H, β -pyrrole), 9.03 (d, 8H, py, $J = 5.8$ Hz), 4.97 (s, 8H, H_1), 2.23 (m, 16H, H_2 , H_7), 1.50 (m, 32H, H_{3-6}), -3.10 (s, 2H, internal NH); ir (potassium bromide): ν 1716.9 (C=O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 424 (20.5), 519 (1.40), 556 (0.56), 585 (0.57), 641 (0.15).

Anal. Calcd. for $\text{C}_{72}\text{H}_{86}\text{N}_8\text{O}_8\text{Br}_4 \cdot 4\text{H}_2\text{O}$: C, 54.60; H, 5.99; N, 7.08. Found: C, 54.80; H, 6.26; N, 7.25.

5,10,15,20-Tetra(*N*-(ethylcarbonylpent-6-yl)pyridinium-4-yl)porphyrin (**1j**).

Alkylation with ethyl-6-bromohexanoate produced **1j** in 64% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 9.56 (d, 8H, py, $J = 6.4$ Hz), 9.23 (s, 8H, β -pyrrole), 9.02 (d, 8H, py, $J = 6.4$ Hz), 4.96 (s, 8H, H_1), 4.11 (m, 8H, $-\text{CH}_2\text{CH}_3$), 2.45 (t, 8H, H_5 , $J = 7.7$ Hz), 2.28 (m, 8H, H_2), 1.75 (m, 8H, H_3), 1.61 (m, 8H, H_4), 1.23 (t, 12H, $-\text{CH}_3$, $J = 7.0$ Hz), -3.10 (s, 2H, internal NH); ir (potassium bromide): ν 1720.7 (C=O), 1157.4 (C-O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 424 (23.6), 519 (1.50), 556 (0.62), 585 (0.68), 641 (0.14).

Anal. Calcd. for $\text{C}_{72}\text{H}_{86}\text{N}_8\text{Br}_4\text{O}_8 \cdot 4\text{H}_2\text{O}$: C, 54.60; H, 5.98; N, 7.08. Found: C, 54.63; H, 5.93; N, 6.56.

General Alkylation Procedure for 5,10,15,20-Tetra(3-pyridyl)porphyrins **2a-j**.

5,10,15,20-Tetra(3-pyridyl)porphyrin (30 mg, 0.05 mmole) was warmed to 100° in anhydrous dimethylformamide under nitrogen. Alkylating agent (2 mmoles) was dissolved in anhydrous dimethylformamide and added slowly to the porphyrin solution. The mixture was refluxed for 4 hours and cooled to 0°. The dimethylformamide was removed by rotary evaporation. Tetraalkylated products were isolated by exhaustive size exclusion chromatography (2:2 cm x 20 cm, 3:1 cm x 40 cm) with methanol.

5,10,15,20-Tetra(*N*-allylpyridinium-3-yl)porphyrin (**2a**).

Alkylation with allyl bromide produced **2a** in 10% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 10.04 (s, 4H, py1), 9.62 (d, 4H, py3, $J = 6.1$ Hz), 9.44 (d, 4H, py5, $J = 6.1$ Hz), 9.26 (s, 8H, β -pyrrole), 8.72 (t, 4H, py4, $J = 6.7$ Hz), 6.45 (m, 4H, H_2), 5.62 (m, 16H, H_3 , H_3 , H_1 , $J = 17.1$, 10.4, 6.7 Hz), -3.14 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 418 (2.41), 514 (1.35), 550 (0.31), 581 (0.52), 636 (0.10).

Anal. Calcd. for $\text{C}_{52}\text{H}_{46}\text{N}_8\text{Br}_4 \cdot 8\text{H}_2\text{O}$: C, 50.08; H, 5.01; N, 8.99. Found: C, 50.14; H, 4.61; N, 8.91.

5,10,15,20-Tetra(*N*-5-hexenylpyridinium-3-yl)porphyrin (**2b**).

Alkylation with 6-bromo-1-hexene produced **2b** in 31% yield as a purple solid; ^1H nmr (dimethyl sulfoxide- d_6): δ 10.15 (s, 4H, py1), 9.70 (d, 4H, py3, $J = 6.5$ Hz), 9.41 (d, 4H, py5, $J = 7.3$ Hz), 9.26 (s, 8H, β -pyrrole), 8.70 (t, 4H, py4, $J = 7.1$ Hz), 5.85 (m, 4H, e), 5.00 (m, 16H, H_6 , H_6 , H_1 , $J = 17.1$, 10.3, 6.5 Hz), 2.19 (m, 16H, H_2 , H_4), 1.6 (m, 8H, H_3), -3.15 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) 418 (20.0), 514 (1.25), 550 (0.37), 581 (0.49), 636 (0.12).

Anal. Calcd. for $C_{64}H_{70}N_8Br_4 \cdot 12 H_2O$: C, 51.67; H, 6.37; N, 7.53. Found: C, 51.76; H, 5.96; N, 7.41.

5,10,15,20-Tetra(*N*-7-octenylpyridinium-3-yl)porphyrin (**2c**).

Alkylation with 8-bromo-1-octene produced **2c** in 50% yield as a purple solid; 1H nmr (dimethyl sulfoxide- d_6): δ 10.12 (s, 4H, py1), 9.69 (d, 4H, py3, $J = 6.7$ Hz), 9.40 (d, 4H, py5, $J = 7.0$ Hz), 9.24 (s, 8H, β -pyrrole), 8.70 (t, 4H, py4, $J = 7.0$ Hz), 5.79 (m, 4H, H_7), 4.93 (m, 16H, H_8 , H_9 , H_{11} , $J = 17.0$, 10.1, 7.0 Hz), 2.20 (m, 8H, H_2), 2.03 (m, 8H, H_6), 1.45 (m, 24H, H_{3-5}), -3.13 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (25.5), 514 (1.44), 550 (0.46), 581 (0.83), 636 (0.20).

Anal. Calcd. for $C_{72}H_{76}N_8O_8Br_4 \cdot 10H_2O$: C, 55.68; H, 6.23; N, 7.21. Found: C, 55.57; H, 6.02; N, 7.34.

5,10,15,20-Tetra(*N*-3-hydroxypropylpyridinium-3-yl)porphyrin (**2d**).

Alkylation with 3-bromo-1-propanol produced **2d** in 67% yield as a purple solid; 1H nmr (dimethyl sulfoxide- d_6): δ 10.12 (s, 4H, py1), 9.69 (d, 4H, py3, $J = 6.7$ Hz), 9.38 (d, 4H, py5, $J = 7.3$ Hz), 9.25 (s, 8H, β -pyrrole), 8.68 (t, 4H, py4, $J = 6.7$ Hz), 5.03 (m, 8H, H_1), 4.89 (s, 4H, OH, deuterium oxide-exchangeable), 3.71 (s, 8H, H_3), 2.38 (t, 8H, H_2), -3.13 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (27.9), 514 (1.49), 550 (0.27), 581 (0.54), 636 (0.06).

Anal. Calcd. for $C_{52}H_{54}N_8O_4Br_4 \cdot 7H_2O$: C, 47.99; H, 5.27; N, 8.67. Found: C, 47.95; H, 5.39; N, 8.36.

5,10,15,20-Tetra(*N*-6-hydroxyhexylpyridinium-3-yl)porphyrin (**2e**).

Alkylation with 6-bromo-1-hexanol produced **2e** in 44% yield as a purple solid; 1H nmr (dimethyl sulfoxide- d_6): δ 10.13 (s, 4H, py1), 9.70 (d, 4H, py3, $J = 6.0$ Hz), 9.41 (d, 4H, py5, $J = 6.4$ Hz), 9.26 (s, 8H, β -pyrrole), 8.70 (t, 4H, py4, $J = 6.5$ Hz), 4.93 (s, 8H, H_1), 4.41 (s, 4H, OH, deuterium oxide-exchangeable), 3.34 (m, 8H, H_6), 2.21 (m, 8H, H_2), 1.47 (m, 24H, H_{3-5}), -3.13 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (29.2), 514 (1.69), 550 (0.38), 581 (0.58), 636 (0.10).

Anal. Calcd. for $C_{64}H_{78}N_8O_4Br_4 \cdot 10H_2O$: C, 50.45; H, 6.49; N, 7.36. Found: C, 50.77; H, 6.19; N, 7.42.

5,10,15,20-Tetra(*N*-8-hydroxyoctylpyridinium-3-yl)porphyrin (**2f**).

Alkylation with 8-bromo-1-octanol produced **2f** in 26% yield as a purple solid 26% yield; 1H nmr (dimethyl sulfoxide- d_6): δ 10.14 (s, 4H, py1), 9.70 (d, 4H, py3, $J = 4.0$ Hz), 9.40 (d, 4H, py5, $J = 6.4$ Hz), 9.25 (s, 8H, β -pyrrole), 8.70 (t, 4H, py4, $J = 6.5$ Hz), 4.94 (s, 8H, H_1), 4.35 (s, 4H, OH, deuterium oxide-exchangeable), 3.29 (m, 8H, H_8), 2.21 (m, 8H, H_2), 1.39 (m, 40H, H_{3-7}), -3.13 (s, 2H, internal NH); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (26.0), 514 (1.69), 550 (0.39), 581 (0.71), 636 (0.11).

Anal. Calcd. for $C_{72}H_{94}N_8O_4Br_4 \cdot 5H_2O$: C, 55.94; H, 6.79; N, 7.25. Found: C, 55.90; H, 6.74; N, 6.95.

5,10,15,20-Tetra(*N*-3-carboxyethylpyridinium-3-yl)porphyrin (**2g**).

Alkylation with 3-bromo-1-proprionic acid produced **2g** in 22% yield as a purple solid; 1H nmr (98% dimethyl sulfoxide- d_6 /2% deuterium oxide): δ 9.95 (s, 4H, py1), 9.46 (d, 4H, py3, $J = 6.3$ Hz), 9.29 (d, 4H, py5, $J = 6.7$ Hz), 9.07 (s, 8H, β -pyrrole), 8.49 (t, 4H, py4, $J = 6.4$ Hz), 5.03 (m, 8H, H_1), 2.92

(t, 8H, H_2 , $J = 6.1$ Hz); ir (potassium bromide): ν 1716.9 (C=O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (26.4), 514 (1.79), 550 (0.64), 581 (0.87), 636 (0.32).

Anal. Calcd. for $C_{52}H_{46}N_8O_8Br_3 \cdot H_2O$: C, 53.42; H, 4.14; N, 9.59. Found: C, 53.36; H, 4.46; N, 9.95.

5,10,15,20-Tetra(*N*-6-carboxypentylpyridinium-3-yl)porphyrin (**2h**).

Alkylation with 6-bromo-1-hexanoic acid produced **2h** in 46% yield as a purple solid; 1H nmr (dimethyl sulfoxide- d_6): δ 10.12 (s, 4H, py1), 9.69 (d, 4H, py3, $J = 5.0$ Hz), 9.39 (d, 4H, py5, $J = 6.7$ Hz), 9.22 (s, 8H, β -pyrrole), 8.69 (t, 4H, py4, $J = 6.8$ Hz), 4.93 (s, 8H, H_1), 2.21 (m, 16H, H_2 , H_5), 1.50 (m, 16H, $H_{3,4}$), -3.13 (s, 2H, internal NH); ir (potassium bromide): ν 1716.9 (C=O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (28.1), 514 (1.67), 550 (0.38), 581 (0.63), 636 (0.30).

Anal. Calcd. for $C_{64}H_{70}N_8O_8Br_4 \cdot 3H_2O$: C, 52.91; H, 5.27; N, 7.71. Found: C, 52.63; H, 5.01; N, 7.60.

5,10,15,20-Tetra(*N*-8-carboxyheptylpyridinium-3-yl)porphyrin (**2i**).

Alkylation with 8-bromo-1-octanoic acid produced **2i** in 38% yield as a purple solid; 1H nmr (dimethyl sulfoxide- d_6): δ 10.12 (s, 4H, py1), 9.66 (d, 4H, py3, $J = 4.0$ Hz), 9.40 (d, 4H, py5, $J = 7.9$ Hz), 9.23 (s, 8H, β -pyrrole), 8.68 (t, 4H, py4, $J = 7.0$ Hz), 4.91 (s, 8H, H_1), 2.19 (m, 8H, H_7), 2.01 (m, 8H, H_2), 1.37 (m, 32H, H_{3-6}), -3.13 (s, 2H, internal NH); ir (potassium bromide): ν 1716.9 (C=O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (26.2), 514 (2.06), 550 (0.66), 581 (0.84), 636 (0.27).

Anal. Calcd. for $C_{72}H_{86}N_8O_8Br_4 \cdot 2H_2O$: C, 55.87; H, 5.86; N, 7.24. Found: C, 55.91; H, 6.37; N, 7.14.

5,10,15,20-Tetra(*N*-(ethoxycarbonylpent-6-yl)pyridinium-3-yl)porphyrin (**2j**).

Alkylation with ethyl-6-bromohexanoate produced **2j** in 30% yield as a purple solid; 1H nmr (dimethyl sulfoxide- d_6): δ 10.16 (s, 4H, py1, $J = 6.4$ Hz), 9.71 (d, 4H, py3, $J = 7.9$ Hz), 9.41 (d, 4H, py5), 9.25 (s, 8H, β -pyrrole), 8.69 (t, 4H, py4, $J = 6.3$ Hz), 4.94 (s, 8H, H_1), 4.00 (m, 8H, $-CH_2CH_3$), 2.35 (t, 8H, H_5 , $J = 7.0$ Hz), 2.22 (m, 8H, H_2), 1.64 (m, 8H, H_3), 1.50 (m, 8H, H_4), 1.11 (t, 8H, $-CH_3$, $J = 7.0$ Hz), -3.13 (s, 2H, internal NH); ir (potassium bromide): ν 1716.9 (C=O), 1198.0 (C-O); uv-visible (water): λ_{max} (nm)/($\epsilon \times 10^4 M^{-1} cm^{-1}$) 418 (24.4), 514 (1.47), 550 (0.66), 581 (0.57), 636 (0.13).

Anal. Calcd. for $C_{72}H_{86}N_8O_8Br_4 \cdot 7H_2O$: C, 52.80; H, 6.16; N, 6.85. Found: C, 52.8; H, 6.55; N, 6.83.

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