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Shape-Selective Ligation to Dendrimer−Metalloporphyrins

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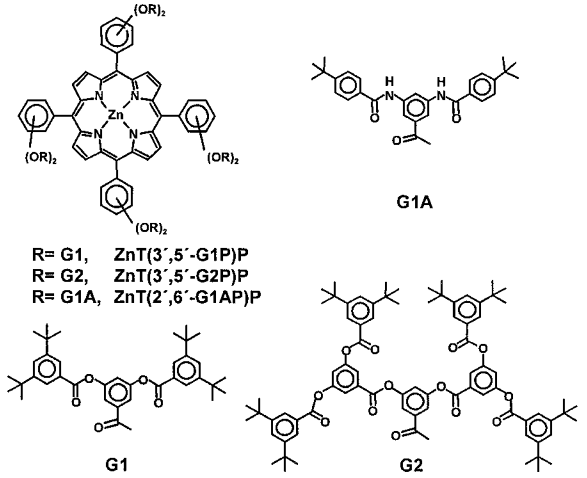
Over the past decade, there has been remarkable progress in the synthesis of dendritic polymers.[1] To generate functional dendritic polymers, there has been an growing interest in incorporation of specific functional moieties either on the surface or in the interior of dendrimers. For example, incorporation of redox metal centers on the exterior of a silane dendrimer led to catalytic oxidation of alkenes[2a] and electrochemical reduction of CO_2 by phosphine dendrimers.[2b] Of particular interest has been the encapsulation of metalloporphyrins into the interior core of a dendritic polymer; such systems have shown interesting photophysical,[3] electrochemical,[4] oxygen binding,[5] and regioselective[6] catalysis. We have previously shown steric effects in dendrimer−metalloporphyrins in access of alkene substrates to the metal during catalytic oxidation.[6] We have now demonstrated dramatic control over ligation of Lewis bases by shape selectivity induced by the dendrimer substituents (dendrons).

Shape control of ligation to functionalized metalloporphyrins and dendrimer−metalloporphyrins has been largely unexplored. While steric control for kinetic processes (e.g., epoxidation of alkenes, hydroxylation of alkanes[7]) has been extensively utilized, modification of equilibrium processes (e.g., axial base ligation) has been less examined. The notable exceptions are the detailed studies of steric control in CO versus O_2 binding[8] and a more limited report of a dendrimer−metalloporphyrin binding a dendrimer ligand.[9] We report here the synthesis, characterization, and shape-selective ligation of dendrimer−metalloporphyrins derived from 2,6-di- and 3,5-di-dendron-substituted *meso*-tetraphenylporphinatozinc(II) complexes.

A series of polyphenyl ester dendrimers (G1 and G2 in Chart 1) and an amide dendrimer (G1A) were synthesized by convergent approach.[6,10] The ester dendrimers, G1 and G2, were appended at all eight *m*-phenyl positions of ZnT(3′,5′-DHP)P, and amide dendrimer, G1A, at all eight of *o*-phenyl positions of the ZnT(2′,6′-DHP)P using a DCC/DPTS coupling reaction[6,10] (Chart 1). ZnT(3′,5′-GnP)P ($n = 1$ and 2) complexes were highly soluble in a variety of organic solvents including alkanes, while ZnT(2′,6′-G1AP)P showed good solubility in polar solvents but only limited solubility in cyclohexane or hexanes. The synthesized dendrimer metalloporphyrins were characterized by UV−visible, ^{1}H NMR, and MALDI-TOF MS spectroscopic techniques. Homogeneity was demonstrated by HPLC and MALDI-MS. Complete synthesis and characterization details are available as Supporting Information.

Chart 1. Chemical Structures of Dendrimer−Metalloporphyrins and Dendrons



The shape selectivities of the binding sites of the Zn dendrimer−porphyrins were probed using the axial ligation of various nitrogenous bases of different shapes and sizes in toluene (Zn porphyrins were chosen because they generally bind only a single axial ligand). On ligation of bases, the visible absorption spectra of Zn dendrimer−porphyrins are red-shifted and show an increase in the extinction coefficient of both the Soret (B) and visible (Q) bands, just as with ZnTPP.[11] As an example, data for titration of ZnT(3′,5′-G1P)P with 4-phenylpyridine are shown in Figure 1. For a series of nitrogenous bases of different sizes and shapes, equilibrium constants (K_{eq}) were evaluated using standard procedures[12] for the Zn dendrimer−porphyrins and ZnTPP (Figure 2).

The K_{eq} values of the ortho-substituted ZnT(2′,6′-G1AP)P were exquisitely sensitive to the shape and size of the substrates. ZnT(2′,6′-G1AP)P binds linear amines (4-phenylpyridine or dodecylamine) as well as the more open pocketed ZnT(3′,5′-GnP)P dendrimer−porphyrins and better than ZnTPP itself. In the case of nonlinear amines, however, differences in K_{eq} of 10^3 to 10^5 were observed among the dendrimer−metalloporphyrins. Surprisingly, the meta-substituted ZnT(3′,5′-GnP)P ($n = 1$, 2) showed a

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[10] (a) Hawker, C. J.; Frechet, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 8405. (b) Abbreviations: ZnT(3′,5′-DHP)P, 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)porphinatozinc(II); ZnT(2′,6′-DHP)P, 5,10,15,20-tetrakis(2′,6′-dihydroxyphenyl)porphinatozinc(II); ZnTPP, 5,10,15,20-tetraphenylporphinatozinc(II); DCC, dicyclohexyldicarbodiimide; DPTS, 4-(dimethylamino)pyridinium 4-toluenesulfonate.[10c] (c) Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65.

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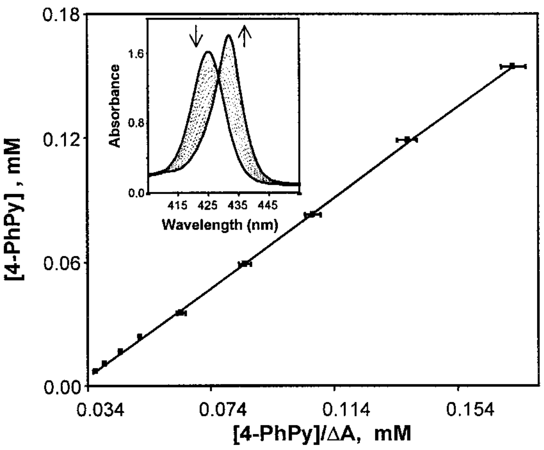

Figure 1. Titration data for binding of 4-phenylpyridine to the dendrimer−metalloporphyrin ZnT(3′,5′-G2P)P in toluene at 25 °C. A plot is given of 4-PhPy concentration vs 4-PhPy concentration divided by the change in absorbance for absorbance changes at 431 nm. Inset shows the visible spectra (Soret region) upon titration with 4-phenylpyridine.

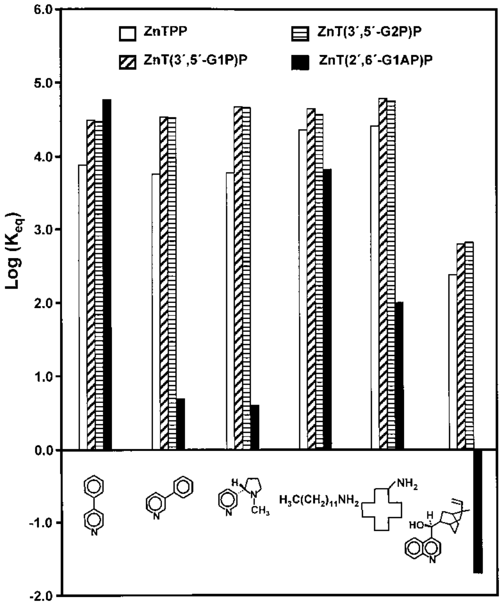

Figure 2. Ligand binding constants for dendrimer-metalloporphyrins relative to ZnTPP. Errors in K_{eq} values are generally less than ±10%; full data are listed in the Supporting Information.

severalfold *increase* in K_{eq} for all the amines relative to ZnTPP. We believe that the increase in binding is primarily due to attractive interactions between the ligand and the aromatic dendrons, since the increase in K_{eq} is more pronounced for the pyridines than for simple alkylamines.[13]

The significant differences in ligand selectivity for the meta- vs ortho-substituted dendrimer−metalloporphyrins are consistent with the differences in the shape of the steric pocket around the Zn center. As shown in Figure 3, molecular modeling studies on free base dendrimer−porphyrins show dramatic changes in the shape of the binding site pocket depending on the position of the dendrimer at the phenyl rings of the porphyrin. In all cases, top access on both faces of the porphyrin is completely limited by the dendrons. Side access, however, is still available. For the meta-substituted dendrimer−porphyrins, $H_2T(3',5'\text{-G1P})P$ and $H_2T(3',5'\text{-G2P})P$, open cavities with diameters of roughly 10 and 7 Å, respectively, permit facile ligation. In contrast, the ortho-substituted $H_2T(2',6'\text{-G1AP})P$ shows only a narrow slit (≈5 Å) suitable for binding of linear substrates only. We believe that the dramatic difference in selectivity for linear vs nonlinear or bulky amines with ZnT(2′,6′-G1AP)P is due to this difference in binding site shape.

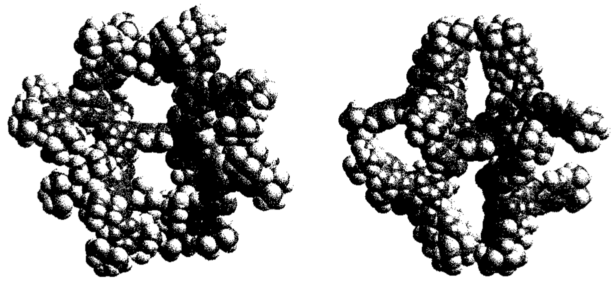

Figure 3. Molecular model side view of the binding sites of (a, left) meta-substituted ($H_2T(3',5'\text{-G1P})P$) compared to (b, right) ortho-substituted dendrimer−porphyrin ($H_2T(2',6'\text{-G1AP})P$). Energy-minimized structures were generated using Cerius v. 2.0 from MSI. Note the open cavity of ≈10 Å vs a narrow slit of ≈5, respectively, which produces a selectivity difference of $>10^4$ in equilibrium binding constants among various amines. In both cases, top access to the porphyrin is completely blocked.

Table 1. Thermodynamic Functions for the Binding of 3-Phenylpyridine to Zn Porphyrins in Toluene[a]

porphyrin	K_{eq}(298 K), mol^{-1}	ΔG°(298 K), kJ/mol	ΔH°, kJ/mol	ΔS°, J/(K·mol)
ZnTPP	5,600 ± 700	−21.3 ± 1.3	−38 ± 2	−59 ± 7
ZnT(3′,5′-G2P)P	32,800 ± 200	−25.9 ± 0.4	−37 ± 1	−38 ± 4
ZnT(2′,6′-G1AP)P	4.8 ± 0.9	−4.2 ± 0.8	−21 ± 2	−56 ± 9

[a] Error estimates are the standard deviations from experimental data; see Supporting Information.

To probe the origin of this shape-selective ligation, thermodynamic functions were determined by measuring the binding of amines to Zn dendrimer−porphyrins as a function of temperature. Specifically, K_{eq} was determined for the binding of 3-phenylpyridine to ZnTPP, ZnT(3′,5′-G2P)P, and ZnT(2′,6′-G1AP)P in toluene over a 40° range, and ΔH° and ΔS° were evaluated from a van't Hoff plot, as shown in Table 1.

The origin of the shape-selective ligation for ZnT(2′,6′-G1AP)P is enthalpic. ZnT(2′,6′-G1AP)P/3-phenylpyridine shows a significantly less negative ΔH°, compared to ZnTPP or ZnT(3′,5′-G2P)P, in keeping with simple ideas of steric constraint in binding the nonlinear 3-phenylpyridine into the tight pocket created by the ortho-dendrons.[14] The more open, meta-substituted dendrimer−metalloporphyrin ZnT(3′,5′-G2P)P shows an increased ΔS° relative to ZnTPP, presumably due to net desolvation of the pocket interior on ligand binding to the Zn.

In summary, a series of bis-pocket dendrimer−metalloporphyrin complexes were prepared with dendron substitution of all eight *o*- or *m*-phenyl positions of 5,10,15,20-tetraphenylporphinatozinc(II). Ligation by various amines with different sizes and shapes was quantitatively measured. Shape-selective ligation was observed with selectivities for linear over nonlinear ligands of more than 10^4.

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Supporting Information Available: Synthesis, characterization, and ligation experimental details of dendrimer−metalloporphyrins (7 pages). See any current masthead page for Web access instructions.

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(13) This increased binding is not strongly solvent dependent. For example, the same increase relative to ZnTPP for ligation of 3-phenylpyridine (i.e., 6-fold) was observed for both toluene and cyclohexane.

(14) (a) For comparison, our parameters for ZnTPP/3-phenylpyridine are similar to those for ZnTPP/pyridine in benzene.[14b] (b) Cole, S. J.; Curthoys, G. C.; Magnusson, E. A.; Phillips, J. N. *Inorg. Chem.* **1972**, *11*, 1024.