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. To generate functional dendritic polymers, there has been an increasing 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 alkene26 and electrochemical reduction of CO2 by phosphine dendrimers.28 Of particular interest has been the encapsulation of metalloporphyrins into the interior core of a dendritic polymer; such systems have shown interesting photo-chemistry, shape-selective ligation of dendrimer-metalloporphyrin complexes were probed using the axial ligation of various nitrogenous bases of different sizes and shapes, equilibrium constants (Keq) were evaluated using standard procedures35 for the Zn dendrimer—porphyrins and ZnTPP (Figure 2).

The Keq values of the ortho-substituted ZnT(2,6′-G1AP)P were extremely 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′-Gn)P dendrimer—porphyrins and better than ZnTPP itself. In the case of nonlinear amines, however, differences in Keq of 105 to 106 were observed among the dendrimer—metalloporphyrins. Surprisingly, the meta-substituted ZnT(3′,5′-Gn)P (n = 1, 2) showed a limited solubility in cyclohexane or hexanes. The synthesized ZnT(3′,5′-G1AP)P, 5,10,15,20-tetrakis(3,5′-dihydroxyphenyl)porphinatozinc(II); ZnT(3′,5′-DHP)P showed good solubility in polar solvents but only limited solubility in cyclohexane or hexanes. The synthesized dendrimer metalloporphyrins were characterized by UV—visible, 1H 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.

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 (ZnPorphyrins 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.13 As an example, data for titration of ZnT(3′,5′-G1AP)P with 4-phenylpyridine are shown in Figure 1. For a series of nitrogenous bases of different sizes and shapes, equilibrium constants (Keq) were evaluated using standard procedures35 for the Zn dendrimer—porphyrins and ZnTPP (Figure 2).

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several fold increase in $K_\text{eq}$ 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 $K_\text{eq}$ is more pronounced for the pyridines than for simple alkylamines.\textsuperscript{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$_2$T(3,5-G1AP)P and H$_2$T(3,5-G2GP)P, open cavities with diameters of roughly 10 and 7 Å, respectively, permit facile ligation. In contrast, the ortho-

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.

Figure 1. Titrination data for binding of 4-phenylpyridine to the dendrimer–metalloporphyrin ZnT(3,5-G2GP)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 $K_\text{eq}$ values are generally less than ±10%; full data are listed in the Supporting Information.

Figure 3. Molecular model side view of the binding sites of (a, left) meta-substituted (H$_2$T(3,5-G1AP)P) compared to (b, right) ortho-substituted dendrimer–porphyrin (H$_2$T(2,6-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 Å, 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$^a$

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>$K_\text{eq}$(298 K), mol$^{-1}$</th>
<th>$\Delta G^\circ$(298 K), kJ/mol</th>
<th>$\Delta H^\circ$, kJ/mol</th>
<th>$\Delta S^\circ$, J/(K·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>5.600 ± 700</td>
<td>−21.3 ± 1.3</td>
<td>−38 ± 2</td>
<td>−59 ± 7</td>
</tr>
<tr>
<td>ZnT(3,5-G2GP)P</td>
<td>32.800 ± 200</td>
<td>−25.9 ± 0.4</td>
<td>−37 ± 1</td>
<td>−38 ± 4</td>
</tr>
<tr>
<td>ZnT(2,6-G1AP)P</td>
<td>4.8 ± 0.9</td>
<td>−4.2 ± 0.8</td>
<td>−21 ± 2</td>
<td>−56 ± 9</td>
</tr>
</tbody>
</table>

$^a$ Error estimates are the standard deviations from experimental data; see Supporting Information.

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\textsuperscript{(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.

\textsuperscript{(14)} (a) For comparison, our parameters for ZnTPP/3-phenylpyridine are similar to those for ZnTPP/pyridine in benzene.\textsuperscript{16} (b) Cole, S. J.; Curthoys, G. C.; Magnusson, E. A.; Phillips, J. N. Inorg. Chem. 1972, 11, 1024.