silyl)benzenide showing the latter to be an appropriate model for the experimentally unobserved dilithiobenzenide.

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Self-Assembly of Porphyrins on Nucleic Acids and Polypeptides

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The free-base porphyrin *trans*-bis(*N*-methylpyridinium-4-yl)-diphenylporphine (*trans*-H_2P_{agg}) organizes under appropriate conditions of concentration and ionic strength, into extended assemblies on single-stranded (ss) and double-stranded (ds) DNA templates.[1,2] The ability to arrange porphyrins into helical domains provides opportunities for the construction of supramolecular-based chemical devices having, for example, useful conduction, magnetic, and catalytic properties. Such applications will require assemblies of metalloderivatives, and in the present report, we consider the effect of metalation on solution and nucleic acid binding properties of this cationic porphyrin. We also present evidence that, in addition to nucleic acid templates, polypeptides can serve to organize these species.

Supramolecular porphyrin structures of the type considered here give rise to unprecedentedly large induced circular dichroism signals in the Soret region.[1,2] We suggested that (1) these signals arise from long-range coupling of transition dipole moments of the porphyrin molecules as they orient on the helical backbone of DNA and (2) this organization is a manifestation of the tendency of *trans*-H_2P_{agg} to aggregate. We consider here the solution properties of *trans*-$Cu^{II}P_{agg}$ and *trans*-$Au^{III}P_{agg}$[3] and report on the CD signals obtained on the binding of these metal derivatives to DNA.

Addition of sodium chloride to an aqueous solution (no DNA added) of *trans*-CuP_{agg} leads to marked spectral changes. There is a large bathochromic shift of the Soret band from 417 to 440 nm with significant hypochromicity and deviation from Beer's law behavior. In these respects, the copper(II) derivative behaves very much like the free-base *trans*-H_2P_{agg} porphyrin (and a number of anionic porphyrins which are known to aggregate in solution[4,5]). In contrast, addition of salt up to 0.2 M has little influence on the spectrum of *trans*-AuP_{agg} and Beer's law is obeyed by this chromophore at the Soret maximum of 401 nm. From these results we conclude that whereas the copper derivative of *trans*-H_2P_{agg} aggregates (as does the nonmetallo form), the gold(III) derivative does not.

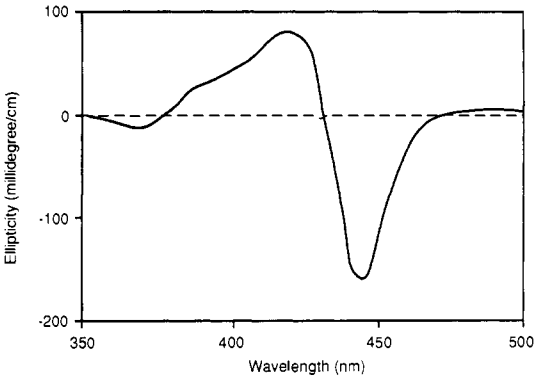

Figure 1. Induced circular dichroism spectra for the *trans*-CuP_{agg}/DNA complex at two different ionic strengths; [*trans*-CuP_{agg}] = 5 μM, [DNA] = 40 μM. At [NaCl] = 0.010 M, a single negative feature is obtained (---) having a magnitude of about 2 mdeg. The signal obtained at [NaCl] = 0.17 M (—) is vastly different in profile and magnitude.

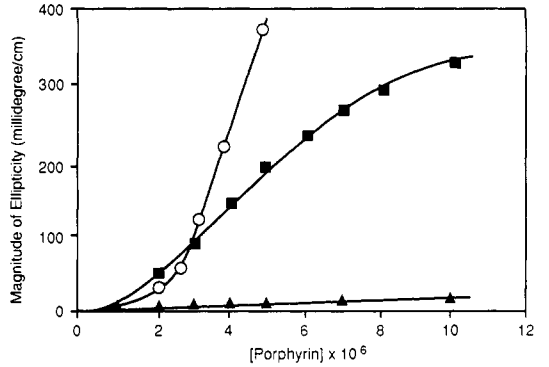

Figure 2. Induced circular dichroism spectra for several porphyrin/DNA complexes as a function of porphyrin concentration: (■) *trans*-H_2P_{agg} at [DNA] = 40 μM, [NaCl] = 0.10 M, λ = 449 nm (negative portion of profile); (○) *trans*-CuP_{agg} at [DNA] = 70 μM, [NaCl] = 0.17 M, λ = 425 nm (positive part of profile); (▲) *trans*-AuP_{agg} at [DNA] = 40 μM, [NaCl] = 0.10 M, λ = 414 nm (at single, negative feature). The concentration dependences of the induced CD signal, S, for the aggregating derivatives can be fit by an equation of the form $S = a[\text{porph}]^n/(1 + b[\text{porph}]^n)$ where $a = 1.33 \times 10^{13}$, $b = 3.05 \times 10^{10}$, and $n = 2$ for *trans*-H_2P_{agg}; $a = 4.15 \times 10^{18}$, $b = 2.93 \times 10^{15}$, and $n = 3$ for *trans*-CuP_{agg}. In contrast, the plot for *trans*-AuP_{agg} is linear, $S = 1.15 \times 10^6$[porph].

Under conditions of low ionic strength, where there is little tendency for charged meso-substituted porphyrins to aggregate,[1,4,5] both metal derivatives, like the parent *trans*-H_2P_{agg}, produce only a single, small negative CD feature in the Soret region *when bound to calf thymus (ct) DNA*. From our previous work with a variety of porphyrins, we have determined that this induced negative CD band is characteristic of an intercalated porphyrin molecular ion.[6] This result parallels those obtained for the Cu(II) and Au(III) derivatives of tetrakis(*N*-methylpyridinium-4-yl)porphine (CuT4 and AuT4).[3,6] However, unlike the results obtained with the nonaggregating CuT4 and AuT4 derivatives, adding salt to the *trans*-H_2P_{agg}/DNA or *trans*-CuP_{agg}/DNA complex leads to dramatic changes in the absorption (about a 15-nm bathochromic shift with some hypochromicity) and CD spectra in the Soret region (see Figure 1). The dependence on porphyrin concentration of the magnitude of the CD signals of *trans*-CuP_{agg}/DNA and *trans*-H_2P_{agg}/DNA is shown in Figure 2. (It is important to note that there is no evidence from CD signals of the DNA polymer light scattering experiments for DNA condensation under these conditions.[1,7]) The nonaggregating *trans*-AuP_{agg} derivative, on the other hand, behaves differently from the *trans*-H_2P_{agg} and *trans*-CuP_{agg} species and instead provides CD signals with DNA much like those of AuT4; i.e., throughout the salt and metallo-

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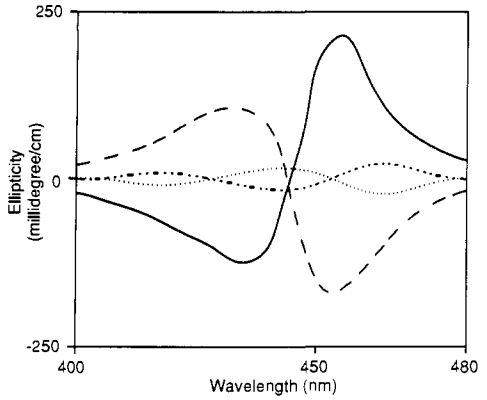

Figure 3. Induced circular dichroism spectra for 5 μM *trans*-H_2P_{agg} in the presence of 50 μM polypeptides at pH 4.5: (•••) poly-D-glutamate, no NaCl added; (– – –) poly-D-glutamate, [NaCl] = 0.1 M; (–•–•–) poly-L-glutamate, no NaCl added; (—) poly-L-glutamate, [NaCl] = 0.1 M.

porphyrin concentrations studied, *trans*-AuP_{agg} appears to remain a monodispersed, intercalated porphyrin. A plot of the CD signal for the *trans*-AuP_{agg}/DNA complex vs concentration of the porphyrin is linear, as shown in Figure 2. Therefore, we conclude that, as observed in solution, *trans*-AuP_{agg} shows little or no tendency to aggregate, even on a DNA surface.

The aggregation model we have proposed for the production of large, conservative CD signals leads to the prediction that ds-DNA is not required by the process. In principle, any helical polymer of repeating, closely spaced negative charges to which *trans*-H_2P_{agg} or *trans*-CuP_{agg} binds should be capable of providing the template needed to produce such unusually large induced CD spectra. The prediction was tested, in part, by using a ss-DNA,[2] but a more convincing test is one in which no nucleic acid is used. To this end, we studied the binding of *trans*-H_2P_{agg} to poly-L- and poly-D-glutamate at pH 4.5, where the polypeptides have been reported as helical.[8] Although the complexes formed with these polypeptides are not as stable as the ones formed with nucleic acids (precipitates appear on standing), freshly prepared solutions produce large, conservative CD signals (Figure 3). It can be seen from Figure 3 that the phase of the signal reflects the helical sense of the polymer; the phases of induced CD of the porphyrin are reversed for the D versus L forms of polyglutamate. Above pH 6, polyglutamate becomes largely random coil albeit with some residual helical character.[9] The induced CD signals of *trans*-H_2P_{agg} with the random-coil polymer (pH 8) are correspondingly significantly smaller, and the phase disposition of the induced conservative porphyrin CD spectrum is opposite to that found when this porphyrin is bound to the same polymer but at conditions where it is predominantly α helix. This may indicate that the structure of the porphyrin aggregate on the random-coil polymer is different or that regions of the random-coil polymer have a helicity opposite to that of its "normal" low pH form.[9]

In conclusion, we offer these results as evidence for the spontaneous formation of supramolecular assemblies on helical templates by selected porphyrins. The tendency of a given porphyrin to aggregate in solution seems to be a useful indicator of the ability of that species to form highly extended assemblies. Kinetic studies to elucidate the mechanism of formation of these porphyrin supramolecular structures are underway.

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Chair-Form Six-Membered Ring Attached Diequatorially to Five-Coordinate Phosphorus. ^1H NMR and X-ray Crystallographic Study

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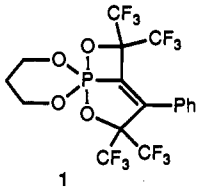
Studies reported over the past few years[1] have emphasized the preference of a 1,3,2-dioxaphosphorinane ring attached to five-coordinate phosphorus to be appended in an apical/equatorial rather than a diequatorial manner. Moreover, in nearly all instances the ring in question was found by ^1H NMR spectroscopy and X-ray crystallography to be in a boat or twist form rather than in a chair conformation. The exceptions were three nearly structurally identical phosphoranes with twist-chair conformations (X-ray results) arising as a result of intermolecular hydrogen bonding.[1a]

Up to now, no X-ray structures showing 1,3,2-dioxaphosphorinane rings attached diequatorially to five-coordinate phosphorus have been reported except for two molecules with the six-membered ring locked in the chair conformation.[2] The increase in energy required to coordinate the ring to phosphorus diequatorially is unknown, although activation free energies for pseudorotations via species with the 1,3,2-dioxaphosphorinane ring diequatorial have been determined.[3,1a,d] Furthermore, there is no information as to what conformation is of lowest energy, chair, twist, or boat.

We report here proof by ^1H NMR and X-ray crystallography for the *diequatorial* attachment of the 1,3,2-dioxaphosphorinane ring of **1** to five-coordinate phosphorus in an essentially trigonal-bipyramidal molecule. Moreover, the conformation of the ring is clearly a *chair* in the crystal; and this conformation is very largely, if not entirely, populated *in solution* as well.

Phosphorane **1** was prepared from reaction of 2-(2-phenylethynyl)-1,3,2-dioxaphosphorinane ($CH_2(CH_2O)_2PC{\equiv}CPh$) with $(CF_3)_2CO$ at −78 °C, a process well-known[4] for other three-coordinate alkynyl-substituted phosphorus compounds, and recrystallized from diethyl ether/pentane, mp 147–148 °C.[5]



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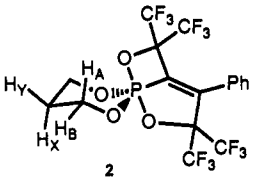

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