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Self-assembly of monopyrazolylporphyrins by hydrogen bonding in solution

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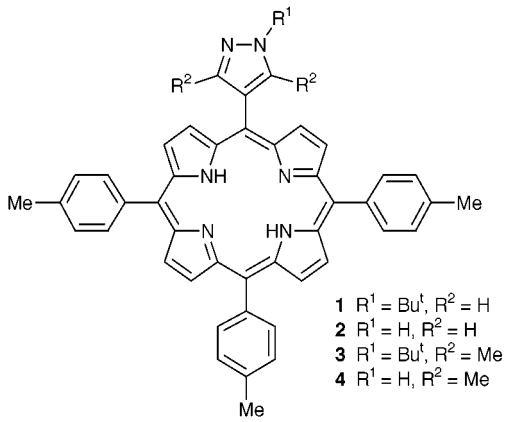
The self-associated structures of two noble *meso*-(monopyrazolyltritolyl)porphyrins synthesized *via* their NH-protected precursors have been studied by ^{1}H NMR, FT-IR and ESI MS measurements; *meso*-(pyrazol-4-yl)porphyrin and *meso*-(3,5-dimethylpyrazol-4-yl)porphyrin form a dimer and a tetramer, respectively, in solution due to intermolecular hydrogen bonding between pyrazole units.

In recent years there has been considerable interest in the construction of porphyrin assemblies of well-organized shape for molecular photonic devices such as artificial light harvesting systems.[1] A self-assembling strategy *via* reversible non-covalent bonding has received much attention and several attempts have been made recently to prepare supramolecular porphyrin arrays.[2–4] Hydrogen bonding is a very useful means of constructing molecular assemblies because it can fix molecules in a particular geometry by virtue of its directionality. Indeed, there are some reports in which assemblies of hydrogen bonded porphyrins have been constructed in both solution[3] and the solid state.[4] The elegance of these systems involves utilizing simple building blocks to establish a well-defined architecture. It is important to prepare novel and simple building blocks for hydrogen bonding which may realize more versatile porphyrin assemblies. In this context, five-membered diazole rings, particularly pyrazole, have been focused on because they have both hydrogen donor and acceptor sites in adjacent positions which can build up a self-complementary hydrogen-bonded assembly. It is well-known that 3,5-disubstituted pyrazoles form a dimer, a cyclic trimer and a cyclic tetramer in the solid state and/or in solution,[5] which motivated us to examine the self-association of pyrazolylporphyrins.

Here we report novel self-assembled dimers and tetramers of porphyrins having 1*H*-pyrazol-4-yl and 3,5-dimethyl-1*H*-pyrazol-4-yl groups, respectively, at the *meso*-position. Porphyrin **2** and **4** were prepared by the conventional Adler–Longo



condensation[6] *via* their pyrazole-NH protected precursors **1** (13%) and **3** (8%) followed by removal of the *tert*-butyl groups in refluxing formic acid to afford the desired porphyrins in moderate yields (81% for **2** and 85% for **4**).

The IR spectra of **2** and **4** recorded in $CDCl_3$ showed strong concentration dependencies. The sharp ν(NH) at 3463 cm^{-1} assignable to pyrazole NH stretching 'free' from hydrogen bonding was weakened upon increasing the concentration, while the broad pyrazole-NH···(N) hydrogen-bonded vibration began to be observed around 3200 cm^{-1} above *ca*. 10^{-2} M. These spectral changes indicate that the formation of hydrogen bonds between pyrazole rings at higher concentrations[7] leads to the porphyrin assemblies. The ESI mass spectra using $CHCl_3$ as eluent showed a peak at *m/z* 1294.1 for **2** and *m/z* 2699.5 for **4**. These two peaks correspond to a dimer of **2** (MW = 1293.6 g mol^{-1}) and a tetramer of **4** (MW = 2699.4 g mol^{-1}), respectively. The peaks of the porphyrin oligomers almost disappeared upon addition of a protic solvent such as MeOH to the eluent, which strongly supports the suggestion that the porphyrin self-assembly is formed by intermolecular hydrogen bonding. In order to confirm the self-assembly of pyrazolylporphyrins, ^{1}H NMR dilution experiments were carried out in $CDCl_3$. In **2** and **4**, appreciable concentration dependencies were observed for the chemical shifts of the pyrazole ring protons, though the pyrazole NH peaks were too broad to be detected under the present experimental conditions.† The proton signal showing the largest concentration dependency was that nearest to the pyrazole NH group, *i.e*. the pyrazole-H3 or -H5 proton of **2** and the pyrazole 3,5-methyl protons of **4**. The magnitude of the dilution shift ($\Delta\delta$) of these protons was 0.033 ppm (downfield shift) for **2** and 0.059 ppm (upfield shift) for **4** upon dilution from 10$^{-3.7}$ to 10$^{-1.5}$ M. These dilution shifts are relatively small but apparently larger than $\Delta\delta$ in the presence of MeOH ($\Delta\delta_{max}$ = 7 × 10^{-3} ppm in $CDCl_3$–CD_3OD = 7:3) and $\Delta\delta$ observed for the corresponding NH-protected **1** and **3** ($\Delta\delta_{max}$ = 6 × 10^{-3} ppm) in $CDCl_3$. The above comparison of ^{1}H NMR spectra has revealed that the concentration depend-

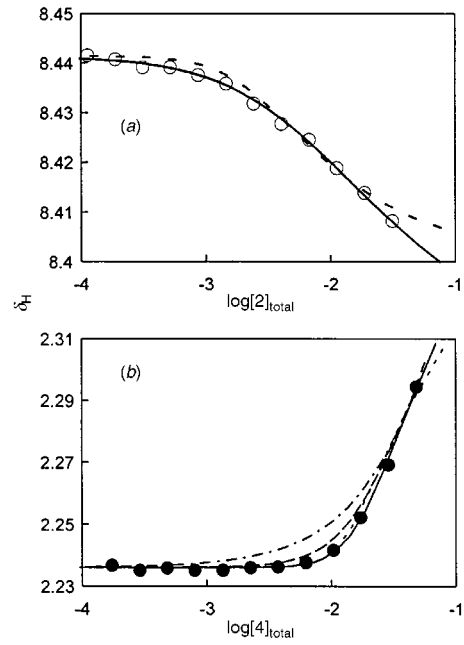
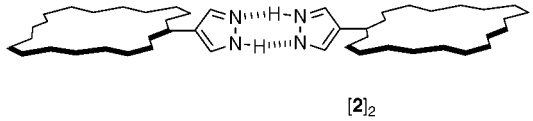
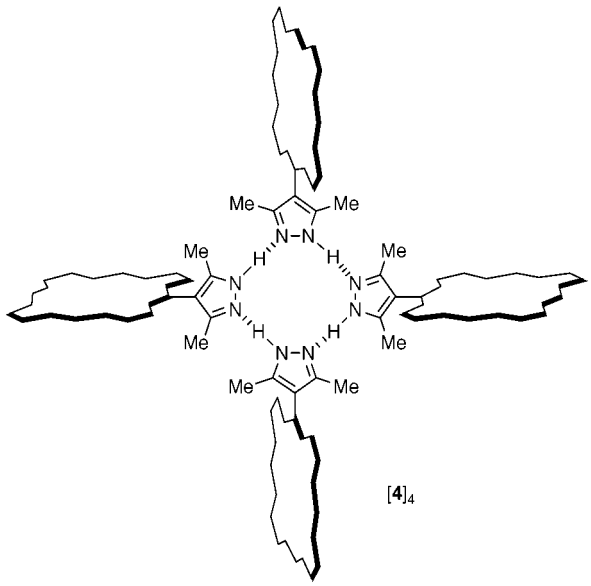


Fig. 1 Curve fitting analysis of ^{1}H NMR dilution shifts in pyrazolylporphyrins: (*a*) (○) pyrazole 3,5-H of **2**, (——) dimer model, (– – –) trimer model; (*b*) (●) pyrazole 3,5-methyl of **4**, (–·–·–·–) dimer model (– – –) trimer model, (——) tetramer model, (·····) pentamer model.

encies observed in **2** and **4** are due to the formation of hydrogen bonds between pyrazole units rather than any other type of aggregation.‡ In order to estimate the possible structure of the association, the dilution curves (at 295 K in $CDCl_3$) were fitted to the models for an equivalent *n*-merization process using nonlinear least-square fitting.[8] The dilution curve for **2** fits well the optimized dimer model throughout the concentration range, but the best-fit trimer model deviates substantially from the experimental data (Fig. 1). On the other hand, the experimental data for **4** fit the tetramer model while they do not obey the dimer, trimer or pentamer model (Fig. 1). The combined ESI MS, IR and NMR results demonstrate that **2** forms a dimer $[\mathbf{2}]_2$



$[\mathbf{2}]_2$



$[\mathbf{4}]_4$

and **4** a cyclic tetramer $[\mathbf{4}]_4$ in $CHCl_3$. There is a report that the hydrogen bonded pyrazole dimer is less stable than the trimer or tetramer.[9] However, porphyrin **2**, in which the rotational barrier of the pyrazole ring is very low,§ seems to prefer the dimer structure (based on molecular modeling), as the aryl groups at the 10 and 20 positions might cause steric hindrance in the case of a co-planer geometry of the pyrazole ring with the porphyrin plane in the trimer or tetramer model. The dimerization constant, $K_2 = 39\ M^{-1}$, obtained from the curve fitting of **2**, is roughly comparable to that in the 2-pyridone system.[10] The tetramerization constant of **4** (K_4) is estimated to be $9.3 \times 10^3\ M^{-3}$ from the curve fitting, which is much larger than that of the hydroxy analogue (*e.g.* phenol).[11] The unique associated structure of the cyclic square is expected to be an interesting building block for porphyrin architecture. Studies in the solid state as well as in solution of pyrazolyl-porphyrins with more than two pyrazole rings, and their metal complexes are currently underway.

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Notes and references

† This is probably due to the electronic quadrupole moment of the nitrogen atom and/or the equilibrium of hydrogen bonding. In the case of pyrazole itself the NH proton can be observed only above *ca.* 10^{-1} M in $CDCl_3$.
‡ The possibility of π–π stacking was excluded because no broadening of the ^1H NMR signals was observed.
§ The rotational barrier of the pyrazole ring in **2** is much lower than that of the *p*-tolyl group: the calculated values are *ca*. 130 and 420 kcal mol^{-1} for the 3,5-unsubstituted pyrazole and the *p*-tolyl groups, respectively (MMX force field).

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