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Cooperative assembly of a double-stranded hydrogen-bonded porphyrin zip

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Abstract—A linear zinc porphyrin dimer has been used for the first time to stabilise two identical non-covalent aggregates by a combination of *N*-pyridyl zinc binding and hydrogen bonding. An improved multigram synthesis of 5,15-bis-(3,5-di-*tert*-butylphenyl)-10,20-bis(trimethylsilylethynyl)porphyrin is described. \bigcirc 2001 Elsevier Science Ltd. All rights reserved.

Porphyrin arrays are attracting attention because of their novel electronic, optical and photophysical properties.¹ Conjugated porphyrins are being investigated as light-harvesting antenna for artificial photosynthetic systems² and for potential applications in sensing,³ opto-electronic⁴ and magnetic materials.⁵ Conjugation in linear porphyrin oligomers is maintained by connecting them with acetylene linkages⁶⁻⁸ and is increased by the assembly of double strands with DABCO which may enhance their non-linear optical behaviour.9 Noncovalent multiple strand arrays also occur in biological macromolecules such as nucleic acid helices and are topical targets for various biomimetic studies.^{10–12} In this paper we report for the first time the use of a linear porphyrin dimer to cooperatively stabilise two hydrogen-bonded 4(3H) pyrimidone dimers in CDCl₃.

The porphyrin dimer **5** required for these studies was prepared by the route shown in Scheme $1.^{13}$ An improved large scale synthesis of a key building block 5,15-bis-(3,5-di-*tert*-butylphenyl)-10,20-bis(trimethylsilylethynyl)porphyrin **2** has been developed.¹⁴ In our hands the previously reported method of preparation involving condensation of trimethylsilylpropynal with a *meso*-aryl dipyrromethane to give **2** directly was unsatisfactory on a larger scale owing to the difficulty of separating porphyrins formed as by-products during the reaction.¹⁵ The acid catalysed scrambling of substituents¹⁶ is a facile process in porphyrin syntheses

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using the trimethylsilylpropynal presumably as a consequence of the ability of the silylacetylene group to assist in stabilisation of a pyrrolic carbocation intermediate. 5,15-Dibromo-10,20-(3,5-di-*tert*-butylphenyl)zinc porphyrin 1 was prepared by standard methods via dipyrrylmethane.¹⁷ This was converted to compound 2 by palladium catalysed ethynylation.^{1,18} Compound 1 did not readily undergo palladium catalysed coupling with triisopropylsilylacetylene so the monoprotected derivative 4 required for dimer formation was prepared following the protocol developed by Anderson.⁹ This involved bis-desilylation with fluoride followed by mono-lithiation with LiHMDS and quenching with triisopropylsilylchloride. Dimer **5** was prepared by acetylenic coupling using Pd(Ph₃P)₂Cl₂.

The association of dimer 5 with 4(3H) pyrimidone was studied by ¹H NMR titration. It was expected that 4(3H) pyrimidone would bind strongly to the zinc porphyrins owing to the known tight binding of DABCO to zinc porphyrins. K values have been reported of 1.8×10^6 and 9.9×10^4 determined in toluene and chloroform, respectively, by UV titration.9 The binding is too strong to be determined by ¹H NMR. An equilibrium between monomer 6 and dimer complex 7 (Scheme 2) was therefore anticipated to be established. Titrating the pyrimidone with aliquots of porphyrin dimer 5 and plotting the chemical shift of the pyrimidone NH versus concentration of the dimer gave a straight line plot which illustrates tight binding of the pyrimidone to dimer 5. The ¹H NMR chemical shift of the pyrimidone NH proton was then monitored as a solution of the expected complex 7 was diluted down (Figs. 1 and 2). The proton moved upfield indicating that the equi-

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Scheme 1. Reagents and conditions: (i) Me_3SiC_2H , $Pd(Ph_3P)_2Cl_2$, CuI, Et_3N , 91%; (ii) MeOH, Bu_4NF , 90%; (iii) LiHMDS then ('Pr)_3SiCl, 48%; (iv) $Pd(Ph_3P)_2Cl_2$ (1.0 equiv.), CuI (1.0 equiv.), Et_3N , 95%.



Scheme 2. Complex formation from porphyrin dimer 5 and 4(3H)pyrimidone.

librium was shifting to a non-hydrogen-bonded complex. The data were analysed by standard methods for an equilibrium of the type $2[C] = [C_2]$.^{19,20} This involves assuming a value for the association constant *K*, calculating a value for the mole fraction of monomer present

as dimer and plotting a graph of mole fraction versus the chemical shift. A straight line graph is obtained with the correct value of K. This gave a value of $K=2500\pm40$ mol⁻¹ ($\Delta G=-4.6$ kcal/mol) for an assumed equilibrium between monomer **6** and dimer **7**.



Figure 1. Plot of the chemical shift against concentration as the [porphyrin 5–4(3H)pyrimidone] complex 7 in CDCl₃ is diluted.



Figure 2. Plot of the chemical shift against mole fraction as the [porphyrin 5–4(3H)pyrimidone] complex 7 in CDCl₃ is diluted.

Comparison of the integrations of the pyrimidone protons and the porphyrin β protons showed that the complex stoichiometry was 1 porphyrin: 2 pyrimidones. Further evidence that the complex 7 exists as the dimer shown and not as a linear polymeric species is provided by comparing the association constant K of 2500 with the association constant for two hydrogen-bonded molecules of 4(3H) pyrimidone. This was determined to be 445±2 mol⁻¹ (ΔG =-3.6 kcal/mol) in CDCl₃ (Figs. 3 and 4).²¹ The pyrimidone NH signal was a sharp peak. The significantly stronger association constant for dimer complex 7 is evidence for cooperative binding which would occur in the cyclic structure but not in an acyclic polymeric complex species. Furthermore it was not possible to determine a value of K for the association of the porphyrin monomer 2-pyrimidone complex into a dimer owing to broadening of the N-H peak which occurred gradually upon addition of porphyrin 2 to 4(3H) pyrimidone. Presumably in the porphyrin 2– pyrimidone complex binding to the zinc atom would increase the acidity of the amide protons and cause peak broadening. However, in the porphyrin 5–pyrimidone complex 7 stronger cooperative aggregation must sharpen the pyrimidone NH signal.

In summary this study illustrates the use of a covalent porphyrin dimer to stabilise two side by side hydrogenbonded aggregates by cooperative assembly. There are further exciting possibilities to use porphyrin ladders for the stabilisation of arrays of hydrogen-bonded aggregates. These studies are in progress.

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Figure 3. Plot of the chemical shift against concentration as 4(3H) pyrimidone in CDCl₃ is diluted.



Figure 4. Plot of the chemical shift against mole fraction as 4(3H) pyrimidone in CDCl₃ is diluted.

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- All new compounds have been satisfactorily characterised by spectroscopic methods and by microanalysis or high resolution mass spectra.
- 14. Typical procedure for 5,15-bis-(3,5-di-tert-butylphenyl)-10,20-bis(trimethylsilylethynyl)porphyrin 2: Dibromoporphyrin 1 (14.0 g, 15.4 mmol) in THF (700 ml) under argon with Pd(PPh₃)₂Cl₂ (600 mg, 0.84 mmol), CuI (150 mg, 0.78 mmol) and trimethylsilylacetylene (6.0 g, 60 mmol) was mixed with freshly distilled triethylamine (35 ml). The mixture was stirred at rt for 16 h, concentrated in vacuo, dissolved up in light petroleum 40-60:dichloromethane (1:1) and filtered through silica. The solution was then concentrated in vacuo and

bis(trimethylsilyl)butadiyne was removed on a vacuum line. The residue was recrystallised from dichloromethane-acetonitrile to yield the title compound (13.2 g, 91%) as a purple powder which had identical spectroscopic properties to those reported previously.⁹

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