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G-quartets as a self-assembled scaffold for circular porphyrin arrays†

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A new lipophilic guanosine carrying a porphyrin chromophore on the ribose moiety has been prepared: evidence is reported for the formation of a supramolecular complex based on G-quartets and containing an array of eight porphyrins.

Understanding and mimicking natural photosynthesis with the goal of producing molecular electronic devices and eventually clean energy is currently one of the areas of major investigation in chemistry.[1]

A particular impetus to the field has been the solution of crystal structures for the reaction centres of photosynthetic bacteria *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides* R-26,[2] as well as the structure elucidation of the antenna complex of *Rhodopseudomonas acidophila*.[3] In particular, the so-called light harvesting system LH2 is an elegant supramolecular assembly in which two distinct sets of 18 and 9 bacteriochlorophylls-a, respectively, are arranged in a circular disposition.

Several synthetic models for such a system have been proposed in the literature, wherein porphyrin arrays were obtained by covalent synthesis.[4] An alternative, and more attractive approach, has been based on the supramolecular strategy of having porphyrin-carrying subunits spontaneously self-assemble to give organised chromophore arrays.[5]

For several years, we have been studying the self-assembly of lipophilic guanosine derivatives in chlorinated organic solvents.[6] These compounds, in the presence of alkali metal ions, form octameric[6b] [Fig. 1(a)] or polymeric[6c] [Fig. 1(b)] species based on the hydrogen-bonded G-quartet.[7] In particular, while 3′,5′-diacyl-2′-deoxyguanosines form octamers or polymers depending on the amount of alkali metal ion added, 5′-acyl-2′,3′-isopropylidene guanosine derivatives form only discrete octamers.[8] The basic structure of the G8 octamer appeared to us to be an ideal non-covalent scaffold for the formation of porphyrin arrays.

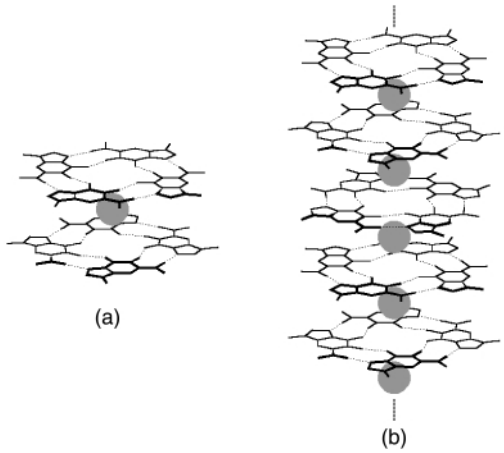


Fig. 1

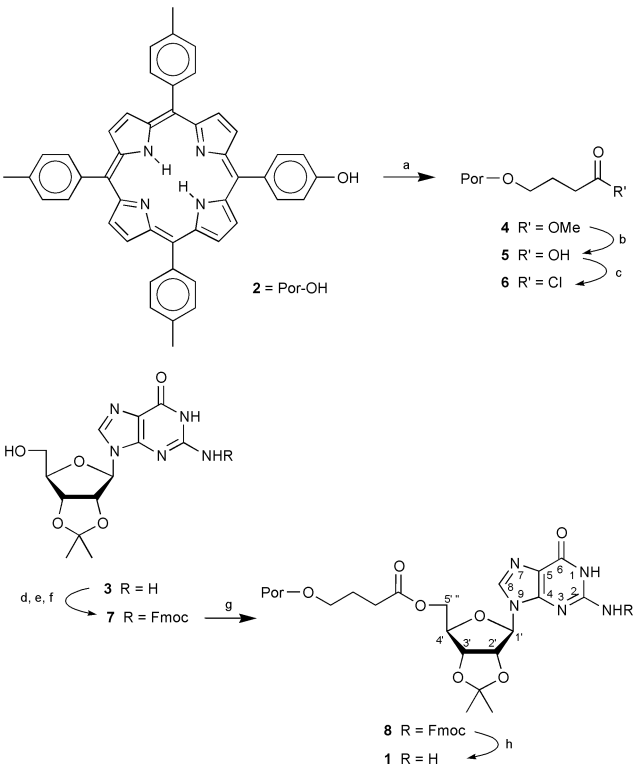
We report here the preparation of a self-assembled porphyrin array consisting of eight chromophores arranged in a circular disposition.

Porphyrin-carrying lipophilic guanosine **1** was synthesized starting from 5-(4′-hydroxyphenyl)-10,15,20-tritolylporphyrin **2**[9] and commercially available 2′,3′-isopropylidene guanosine **3** according to Scheme 1.

Hydroxyporphyrin **2** was alkylated with 4-bromobutyric acid methyl ester, and the resulting ester **4** (93%) was then hydrolysed to give carboxylic acid **5** (95%), which was converted into the corresponding acyl chloride **6**.

Isopropylidene guanosine **3** was converted into the *N*(2)-Fmoc derivative **7**[10] (56%) and condensed with porphyrin acid chloride **5** to give ester **8** (31%). Deprotection of ester **8** gave the porphyrin-functionalised guanosine **1** (76%). All of the compounds were characterized by NMR, ESI mass spectrometry and elemental analysis (ESI†).

Derivative **1** self-assembles in chloroform in the presence of potassium picrate giving rise to octamers consisting of two G-quartets, as inferred from UV–VIS, CD, 1D and 2D ^{1}H NMR studies.



Scheme 1 *Reagents and conditions*: (a) $BrCH_2CH_2CH_2CO_2Me$, K_2CO_3, DMF; (b) KOH, dioxane, MeOH, H_2O, 80 °C then dil. AcOH; (c) $SOCl_2$, THF, reflux; (*d*) Me_3SiCl, pyridine; then (e) FmocCl then (f) H_2O; (g) **6**, CH_2Cl_2, pyridine; (h) piperidine, CH_2Cl_2.

† Electronic supplementary information (ESI) available: 1. ESI-MS spectrum of **1** in methanol–dichloromethane and elemental analysis results. 2. ^{1}H NMR and NOESY spectra (400 MHZ) of 2 mM $[\mathbf{1}]_8$–Kpic in $CDCl_3$ at −10 °C. 3. Tentative structure of the octameric complex, as evinced from preliminary data. See http://www.rsc.org/suppdata/cc/b0/b006160n/

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Proton NMR spectra (ESI†) show the characteristic features of G-quartet formation upon K^+ complexation. Thus, the broad singlet at 6.37 ppm for the N(2)H2 splits into two signals centred at 9.69 ppm [H-bonded N(2)H] and 6.43 ppm [free N(2)H], respectively, at −10°C. These separate signals for the exocyclic amine, already visible although broader at room temperature, are diagnostic of G-quartet formation.[13] The NOESY spectrum shows cross peaks among both these N(2)H2 protons and the N(1)H imino proton at 12.52 ppm.[6b,13] Conversely, there is no significant shift of any other signal in the ^{1}H NMR spectrum upon complexation.[14]

In the present case, the nucleoside protons for porphyrin-functionalised guanosine **1** are not split upon K^+ coordination, as was previously observed for the 3′,5′-diacyl deoxyG-derivatives,[6a,b] and NMR data indicate an exclusive *syn* conformation of the nucleobases around the glycosidic bond (*e.g.* a strong NOE cross peak between H8 at 7.31 ppm and H1′ at 6.04 ppm). So far, all the 5′-alkanoyl-2′,3′-isopropylidene G derivatives that we have investigated have behaved in this way.[8]

The visible spectra of ester **4** and derivative **1** in $CHCl_3$ before K^+ extraction are nearly superimposable, as would be expected if no electronic interaction between the guanine and porphyrin chromophores takes place.[5a] In addition, the spectrum of **1** after K^+ extraction does not change, ruling out a self-assembling process in which porphyrin stacking is involved. This stacking in fact would lead to strong electronic interactions with consequent modification of the absorption. The stoichiometric ratio of 8 molecules of derivative **1** per picrate ion can be deduced from quantitative absorption measurements.

The CD spectra of **1** before and after complexation with K^+ picrate are shown in Fig. 2. Before K^+ extraction, the signal is very weak and no exciton couplets can be observed. Complexation of the cation produces a dramatic effect in the CD spectrum, as exciton couplets appear both in the guanine absorption region (*ca.* 270 nm) and in the Soret region (*ca.* 417 nm). While the couplet centered at 270 nm is diagnostic of the assembly of guanine bases into an octamer,[11] that corresponding to the Soret band indicates a weak, intermolecular, electronic interaction between porphyrin chromophores:[12] this demonstrates that porphyrins are disymmetrically arrayed around the $[G]_8K^+$ complex. The relatively low intensity of this signal is likely to be due to the conformational freedom of the porphyrin chromophores, which are attached by flexible linkers to the G-quartet platforms.

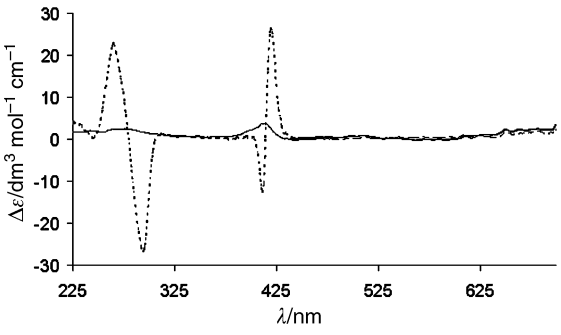

Fig. 2 CD spectra of **1** (0.3 mM in $CHCl_3$) before (——) and after (·····) K^+ extraction.

In conclusion, we have synthesized a new porphyrin derivative which responds to K^+ ions by forming a supramolecular array of eight porphyrins with a circular disposition (see ESI for a tentative structure†). The detailed stereochemistry of the aggregate is now under investigation, as well as the photochemical energy transfer processes possible in this octameric system. Preparation of new derivatives capable of forming aggregates with a larger number of porphyrins arranged circularly around the G-quartets is also being pursued.

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