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Hexakis (pyridyl-functionalised porphyrinato)benzene as a building block for the construction of multi-chromophoric arrays

Marga C. Lensen,[a] Mariangela Castriciano,[b] Ruud G. E. Coumans,[a] Jantien Foekema,[a]
Alan E. Rowan,[a,]* Luigi Monsù Scolaro[b] and Roeland J. M. Nolte[a]

[a]*Department of Organic Chemistry, NSRIM, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*
[b]*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone n.31 V.ll. S. Agata 98166 Messina, ISMN-CNR, Sezione di Messina, and INFM, Unità di Messina, Messina, Italy*

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Abstract—A new hexakis porphyrinato benzene compound has been synthesised and studied by different spectroscopic techniques. It consists of 6 porphyrin moieties which are covalently attached to one central benzene core. Each porphyrin contains 3 pyridyl functions, making a total of 18 potential coordination sites. The structure is a multi-porphyrin array in its own right but can be extended further by means of metal-directed self-assembly. This was demonstrated with the help of a platinum diimine complex substituted with two dodecyl-tails. The pyridine-functionalised hexa-porphyrin was found to bind only 6 instead of the expected 18 platinum complexes, which is ascribed to steric hindrance. Electron microscopy studies reveal that both the pyridine-functionalised hexaporphyrin and its metal-coordination product form well-defined ring structures of micrometer size on solid supports.

Arrays of chromophoric molecules are currently attracting much attention in connection with the design and construction of artificial light-harvesting systems. In order to obtain architectures with well-defined shape and size, porphyrins are very versatile building blocks. The synthetic accessibility, the usually high stability and the interesting and peculiar spectroscopic properties of this class of molecules have been exploited in their use as components of nanometric scale photonic devices. Especially, the physico-chemical features are strictly related to their aggregation state and strongly depend on the microstructural environment.[1]

Porphyrin arrays can be obtained through different methodologies, i.e. by covalent coupling reactions or by non-covalent self-assembly. The covalent approach has led to interesting arrays,[2–5] the major disadvantages being the often troublesome synthesis and the problems in the purification of the products due to low solubility. The non-covalent, supramolecular approach is a promising alternative. Taking advantage of molecular recognition effects and by applying kinetically labile coordination bonds, defect-free structures due to the self-correcting nature of the non-covalent interactions can be achieved.[6] Interesting examples of multi-porphyrin arrays which are built up by metal-coordination[7,8] or are held together by multiple hydrogen bonds[9] have been recently reported. A variety of two- and three-dimensional porphyrin architectures has been described, e.g. rings,[10] squares,[11] tapes,[12] sieves,[13] windmills,[14] and star-shaped arrays.[15]

In a previous paper we reported on the synthesis and self-assembling properties of hexakis porphyrinato benzene compounds, which were found to form large ring-shaped nanostructures on various substrates.[16] The construction of these rings is a combination of two of the above mentioned approaches: covalent synthesis of the porphyrin hexamer and non-covalent synthesis of the rings by a combination of self-assembly and aided assembly processes.[17] As an extension of this work we report here on the synthesis of a hexakis (pyridyl-functionalised porphyrinato)benzene compound **2** which was designed to be extended to multi-chromophoric superstructures by metal-directed self-assembly. In this paper we describe the coordination of a (bis)dodecyl-substituted diimine platinum complex **3** to compound **2**. By employing the strategy previously used to obtain a tetra-nuclear platinum(II) complex containing tetrakis(4-pyridyl)porphyrin as a core ligand,[18,19] the porphyrin hexamer can, in principle, be functionalised with up to 18 platinum complexes.

Keywords: supramolecular chemistry; metal-directed self-assembly; porphyrin arrays; nanostructures.

* Corresponding author. Tel.: +31 24 365 2323; fax: +31 24 365 2929; e-mail: rowan@sci.kun.nl

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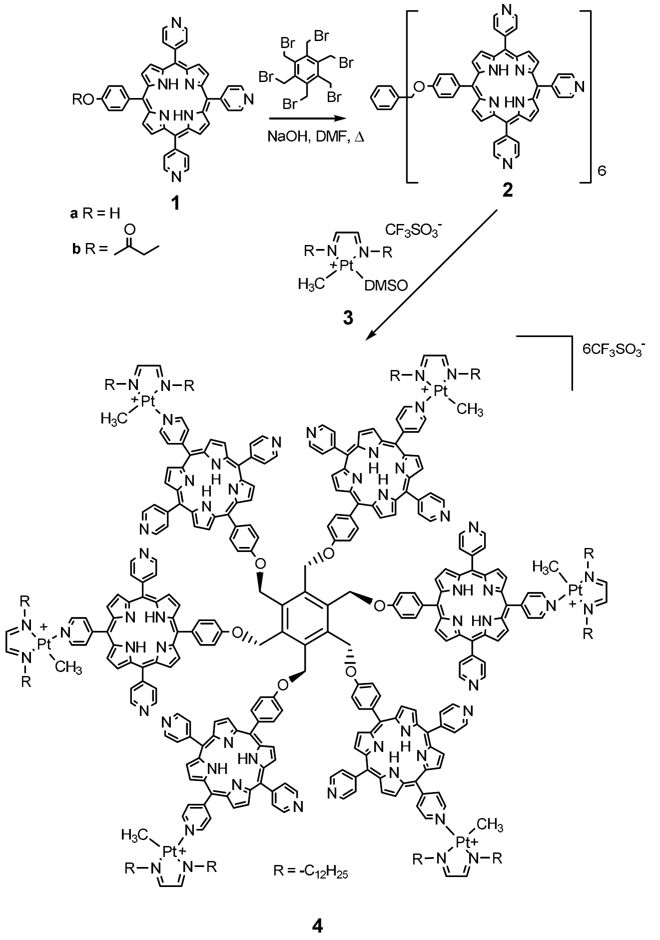
Compound **2** was synthesised following the procedure reported in Scheme 1. The product was soluble in organic solvents and purified by column chromatography. NMR and mass spectrometry of **2** confirmed the formation of the hexameric species.

The introduction of the platinum molecular fragment can be followed by titrating a solution of hexamer **2** with the sulfoxide complex **3**. The UV–vis spectra of compound **2** in chloroform solution exhibited a Soret band centred at 419 nm, which is bathochromically shifted in the final platinated compound ($\Delta\lambda = +$ 10 nm). The UV–vis titrations (Fig. 1a) displayed a gradual, nearly two-step conversion, which leveled off after the addition of six platinum equivalents, indicating that only six platinum diimine units are connected to the porphyrin hexamer in the final product **4** and not the expected 18.

^{1}H NMR measurements were carried out on this final product, which supported the formation of the 6- rather than 18-fold substituted complex. A general broadening of all the resonances was a further evidence of the conversion of compound **2** to **4**. Full details concerning the NMR measurements will be presented elsewhere.



Scheme 1.

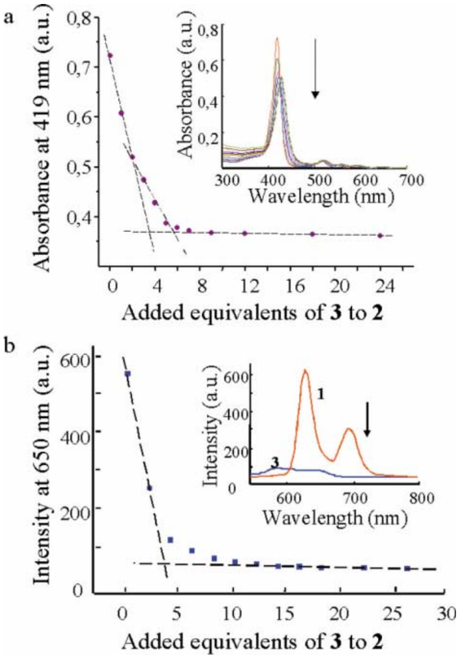


Figure 1. (a) UV–vis and (b) fluorescence emission titration ($\lambda_{exc.} = 420$ nm) of a solution of **2** in $CHCl_3$ with **3** in $CHCl_3$.

The addition of **3** to a solution of **2** in chloroform led to a decrease of the fluorescence intensity of the hexakis pyridylporphyrinato compound. Monitoring the fluorescence decrease showed that the spectral changes, i.e. decrease of emission intensity, predominantly occurred during the addition of the first three equivalents of platinum diimine complex (Fig. 1b). This suggests, that it takes a maximum of 2–4 platinum ligands per hexa-porphyrin molecule to completely quench the fluorescence.

This result can be understood by taking into account the conformation of this class of hexakis porphyrinato benzenes in solution. Previous molecular modelling and NOE-NMR studies have shown that the hexakis porphyrinato molecules are preferentially propeller-shaped and that the six porphyrins stack two by two to form three pairs.[16] The propeller-like geometry is also adopted by the pyridyl-functionalised hexakis porphyrinato benzene **2** as was clearly confirmed by the observed chemical shift changes upon going from porphyrin **1b** to **2** (see Fig. 2). This was further confirmed by 2D-NOESY which revealed strong contacts between the *cis*-pyridyl protons and the central NH- protons similar to that seen previously. These findings suggest that only the pyridyl groups in *trans* positions with respect to the ether linkage can coordinate a platinum center, due to the steric hindrance induced by the overlap of the porphyrin planes. In such dimeric pairs electronic interactions will also occur. Apparently, the excitation energy of one porphyrin unit can be easily transferred to another porphyrin that contains a coordinated platinum complex and can act as a quenching site (heavy atom effect[20]). Hence, due to the adopted geometry the fluorescence emission is quenched either by a coordinated Pt metal or the Pt metal of its dimeric partner.

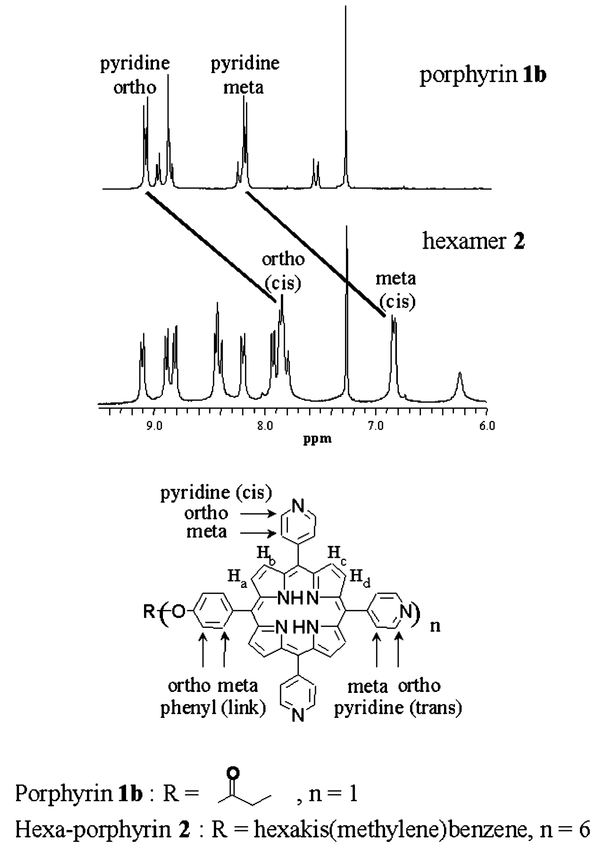


Figure 2. ^1H NMR spectra of porphyrin **1b** and hexakis porphyrinato benzene **2** in $CDCl_3$ including designations of the protons.

Comparison of the UV–vis spectrum of hexamer **2** with that of monomeric porphyrin **1b** in chloroform revealed a broadened Soret band at 418 nm (Fig. 3a). Upon dilution the absorption maximum of **2** shifted to 426 nm. This result can be explained by assuming that in a concentrated solution intermolecular stacking of molecules of hexamer **2** occurs in a face-to-face manner. Diluting the solution disrupts this inter-hexamer aggregation and the internal stacking of the porphyrins within one hexamer becomes visible. This intramolecular stacking occurs in an edge-to-tail geometry, which results in a red-shifted Soret band. The addition of ethanol to a diluted solution of **2** in chloroform made the Soret band shift back to 419 nm and a sharpening of this band was again observed (Fig. 3b). This implies that the intermolecular aggregation of the hexa-porphyrin molecules occurs in a face-to-face manner.

Resonance light scattering (RLS) experiments[21] were carried out on a chloroform solution of the hexamer **2**. The spectra did not show a detectable enhancement of the signal in correspondence to the Soret region of the compound. This finding together with the UV–vis spectra suggest the presence of dimers or small oligomers. RLS spectra on an acetone solution of the platinated hexamer **4** were strongly modulated by the absorbance of the sample, and did not evidence resonant peaks, exhibiting a rather low intensity with respect to the neat solvent, in line with the monomeric nature of this compound in acetone.

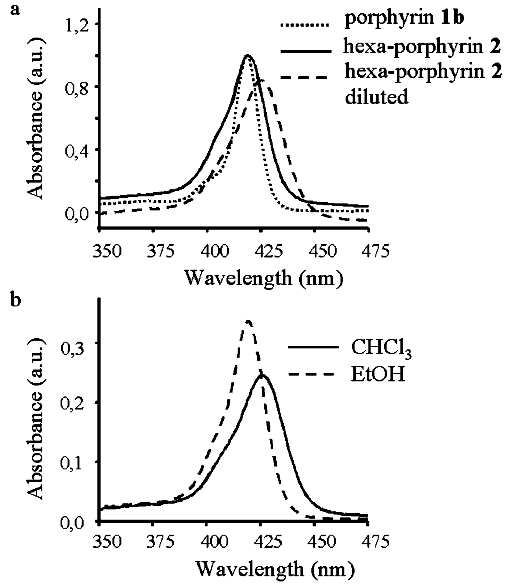


Figure 3. (a) UV–vis spectra of porphyrin **1b** and hexakis porphyrinato benzene **2** in $CHCl_3$ (10^{-6} M). The spectra are normalised. (b) UV–vis spectra of **2** in $CHCl_3$ and in ethanol (10^{-6} M).

The self-assembling properties of the hexakis pyridylporphyrinato benzene molecules on surfaces were studied by transmission electron microscopy (TEM). A chloroform solution of **2** (10^{-6} M) was spread on a carbon-coated copper grid. TEM studies revealed the presence of micrometer-sized rings comparable to those observed previously by us for related compounds.[16] In a similar experiment, the platinum-substituted hexa-porphyrin complex **4** (10^{-6} M in acetone) was allowed to self-assemble on carbon-coated copper grids. Also in this case the ring-shaped aggregates were observed by TEM (Fig. 4). Apparently, the presence of multiple charges (6) do not disrupt the (mainly π–π stacking) interactions between the molecules which account for the self-assembly behaviour of **4**. We are currently investigating these nano-structures in more detail and intend to develop them further as special types of heterogeneous catalysts.

In summary, we have synthesised a new array of 6 porphyrins with pyridine functions which can coordinate to metal complexes. The metal-directed self-assembly of this porphyrin species with platinum diimine complexes yields a 1:6 complex in which the six platinum complexes are coordinated to the pyridine substituents at the periphery of the hexameric porphyrin molecule. Both the platinated product and the uncomplexed porphyrin hexamer form well-defined, micrometer-sized ring structures on solid supports.

Synthesis of ***2***: To a mixture of **1a** (48 mg, 0.075 mmol) in 3 ml DMF was added ground NaOH (7.8 mg, 0.19 mmol) under a nitrogen atmosphere. After stirring the

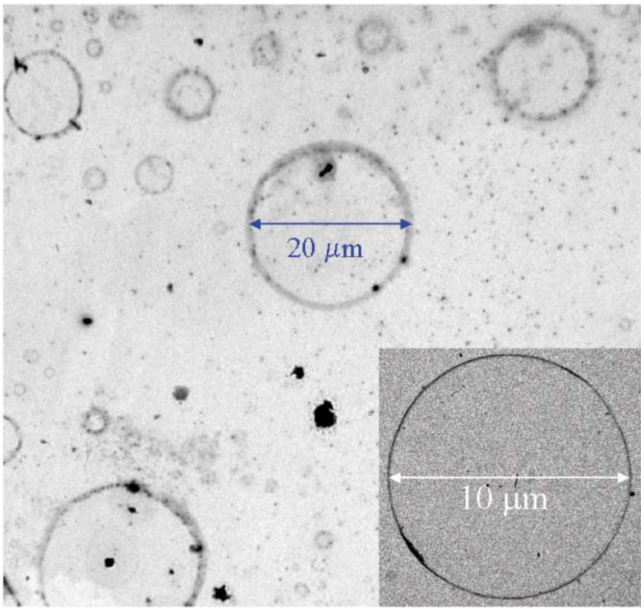


Figure 4. TEM image of a sample of compound **4** obtained by evaporation of a 10^{-6} M solution in acetone on a carbon-coated copper grid. Inset: hexakis pyridylporphyrinato benzene **2**.

mixture at room temperature for ca. 30 min a green solution was obtained. To this solution was added hexakis bromomethylbenzene (5.5 mg, 8.6 μmol) and the mixture was heated overnight at 90°C under exclusion of light. The solution was neutralised using aqueous 1N HCl and a saturated $NaHCO_3$ solution. The product was extracted with CH_2Cl_2 and the solution was concentrated. After evaporation of the solvent, the crude purple product was subjected to column chromatography (silica 60H, eluent: $CHCl_3/NEt_3/EtOH$ 197/3/10, v/v/v). Yield 10.2 mg (30%); ^1H NMR ($CDCl_3$, 200 MHz): δ 9.10 (d, 12H, pyridyl, $J=5.7$ Hz), 8.85 (d, 12H, pyrrole, $J=4.8$ Hz), 8.81 (d, 12H, pyrrole, $J=4.8$ Hz), 8.43 (d, 12H, pyrrole, $J=4.7$ Hz), 8.40 (d, 12H, phenyl, $J=7.6$ Hz), 8.21 (d, 12H, pyridyl, $J=5.7$ Hz), 7.92 (d, 12H, pyrrole, $J=4.9$ Hz), 7.85 (d, 24H, pyridyl, $J=5.1$ Hz), 7.80 (d, 12H, phenyl, $J=7.6$ Hz), 6.84 (d, 24H, pyridyl, $J=5.0$ Hz), 6.24 (br, 12H, benzylic) ppm; ^{13}C NMR (75 MHz): δ 159.0 (6C *ipso* to OCH_2), 149.8 (*t*-pyridyl; 6C *para* to N), 149.0 (*c*-pyridyl; 12C *para* to N), 148.4 (*t*-pyridyl; 12C *ortho* to N), 147.3 (*c*-pyridyl; 24C *ortho* to N), 138.8 (6C benzene core), 135.6 (phenyl; 12C *meta* to O), 135.0 (phenyl; 6C *para* to O), 134–129 (br, 96C α- and β-pyrrole), 129.4 (*t*-pyridyl; 12C *meta* to N), 128.3 (*c*-pyridyl; 24C *meta* to N), 120.7 (6 mesa C phenyl-link), 117.2 (6 mesa C *t*-pyridyl-link), 116.9 (12 mesa C *c*-pyridyl-link), 113.2 (phenyl; 12C *ortho* to O), 64.6 (6C benzyl) ppm; MS (HR-MALDI-TOF): $M^+=3949.56$ (m/z); calcd for $C_{258}H_{168}N_{42}O_6$: $M_w=3949.41$; UV–vis ($CHCl_3$): $\lambda=419$, 514, 548, 588, 648 nm. Fluorescence emission ($CHCl_3$): $\lambda_{exc.}=420$ nm, $\lambda_{em.}=650$, 726 nm.

Synthesis of **4**: Complex **3** (16 mg, 0.02 mmol) was added under stirring to **2** (4.5 mg, 1.1 μmol) dissolved in 10 ml of chloroform. The solution was allowed to react overnight. The compound was precipitated by first adding diethyl ether and then cooling at 0°C overnight. The dark red solid was filtered, washed with small portions of ice-cold diethyl ether, and dried under vacuum for 12 h. Yield 80%; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.4–7.9 (br, ArH), 6.4 (br, 12H, $-OCH_2-$), 4.2 (m, 12H, $-NCH_2-$), 4.0 (m, 12H, $-NCH_2-$), 1.9–0.4 (br, alkyl) ppm; UV–vis (acetone): $\lambda=429$, 522, 554, 592, 650 nm.

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