

A mutually perpendicular phthalocyanine pentamer obtained by a one-step reaction

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A phthalocyanine pentamer consisting of mutually orthogonal Pc units has been prepared by a one-step reaction using oxo(phthalocyaninato)titanium(IV) and 2,3,9,10,16,17,23,24-octahydroxyphthalocyanine and characterized by mass, electronic absorption and magnetic circular dichroism spectroscopy and gel-permeation chromatography.

In contrast with the porphyrins, it is difficult to control steric interactions with the phthalocyanines (Pcs). Accordingly, most reported poly-Pc structures are limited to a few well-known types: one dimensional stacked μ -oxo SiPcs, liquid crystalline Pcs, cofacial rare earth sandwich Pcs, and planar dimers.¹ In addition, controlling the relative orientation of Pc units in Pc multimers is much more difficult than for porphyrins, since Pcs are generally obtained by template reactions and many peripheral substitution patterns are conceivable.¹ In this communication we report the first example of a Pc pentamer, in which four peripheral Pc units are covalently bound, and orthogonal to, a central Pc, $\text{H}_2\text{Ti}_4\text{Pc}_5$ (Scheme 1).

In synthesizing $\text{H}_2\text{Ti}_4\text{Pc}_5$, we utilized the reactivity of the axial oxygen in TiOPc , which is readily displaced by *ortho*-phenolic OH groups, with the elimination of water, to produce two ether linkages.² Thus, an excess of tetra-*tert*-butyl TiOPc , obtained by a literature procedure,³ was reacted with 2,3,9,10,16,17,23,24-octahydroxy H_2Pc^4 in dichloromethane at rt for several days (Scheme 1),^{2b} and the mixture was imposed on a gel permeation column (Bio-beads SX-1, Bio-Rad), using

the same solvent as eluent. The first green fraction was collected. Although this portion did not give a clear NMR spectrum due to poor solubility, satisfactory elemental analyses were obtained. Time-of-flight mass spectrometry showed $m/z = 3774$, which corresponds to the structure of $\text{H}_2\text{Ti}_4\text{Pc}_5$ (calcd. for $\text{C}_{224}\text{H}_{202}\text{N}_{40}\text{O}_8\text{Ti}_4 = 3773.46$), together with cluster of peaks at *ca.* $m/z = 2977$, 2207, and 1495 (Fig. 1).⁵ The difference between each peak corresponds to *ca.* one Pc unit. Since this mass spectrum could also be obtained from a mixture of compounds consisting of two to five Pc units, the elution time of $\text{H}_2\text{Ti}_4\text{Pc}_5$ in gel-permeation chromatography was compared

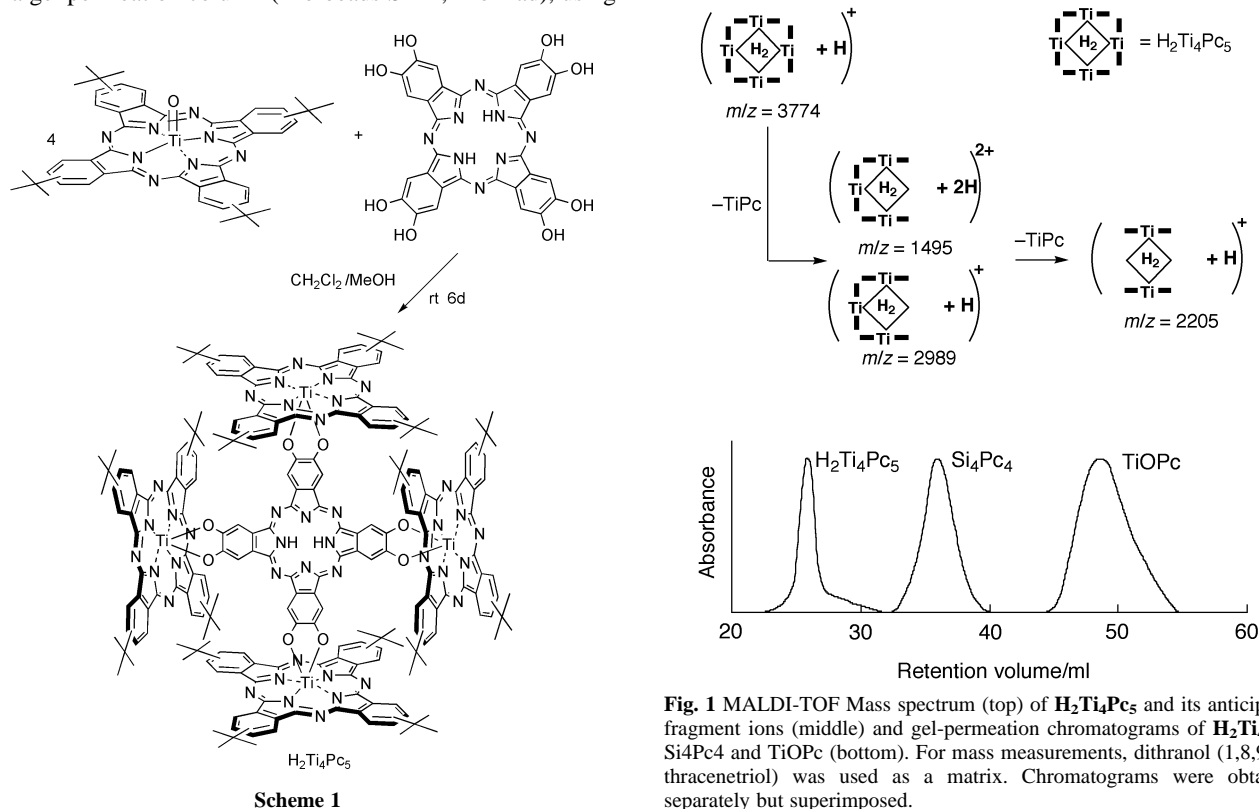


Fig. 1 MALDI-TOF Mass spectrum (top) of $\text{H}_2\text{Ti}_4\text{Pc}_5$ and its anticipated fragment ions (middle) and gel-permeation chromatograms of $\text{H}_2\text{Ti}_4\text{Pc}_5$, Si_4Pc_4 and TiOPc (bottom). For mass measurements, dithranol (1,8,9-anthracenetriol) was used as a matrix. Chromatograms were obtained separately but superimposed.

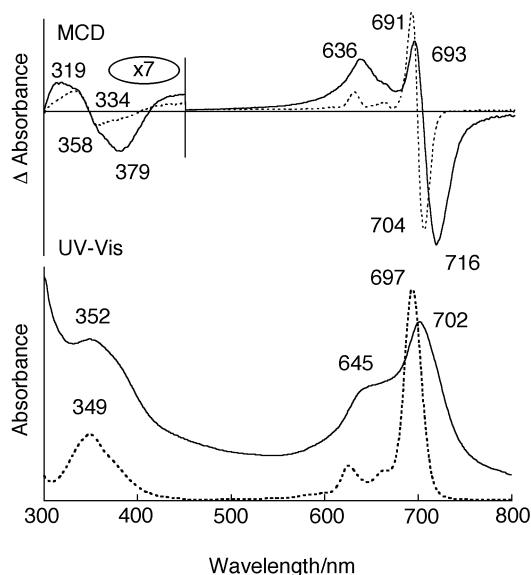


Fig. 2 Electronic absorption (bottom) and MCD (top) spectra of $\text{H}_2\text{Ti}_4\text{Pc}_5$ (solid lines) and *tert*-butylated TiOPc (dotted lines) in dichloromethane.

with those of tetra-*tert*-butylated TiOPc and μ -oxo tetramer⁶ of tetra-*tert*-butylated SiPc (*i.e.* Si_4Pc_4). $\text{H}_2\text{Ti}_4\text{Pc}_5$ showed a single sharp peak, confirming the presence of a single compound. In addition, the shorter elution time of $\text{H}_2\text{Ti}_4\text{Pc}_5$ (elution speed in column = 1.59 cm min^{-1}) indicated that $\text{H}_2\text{Ti}_4\text{Pc}_5$ ($M_w = 3773.89$) is volumetrically larger than Si_4Pc_4 ($M_w = 3142.21$) (elution speed in column = 1.14 cm min^{-1}), in agreement with the proposed structure. The mass spectroscopy and gel-permeation chromatography results clearly indicate the formation of a pentamer, corresponding to $\text{H}_2\text{Ti}_4\text{Pc}_5$. Although we have been unable to obtain crystals suitable for X-ray diffraction, an arrangement in which all Pc units are mutually orthogonal seems most likely, since only the Ti=O functionality can react with hydroxy groups of the octahydroxy H_2Pc to form the pentamer.

Fig. 2 shows electronic absorption and magnetic circular dichroism (MCD) spectra of tetra-*tert*-butylated TiOPc mono-

mer and $\text{H}_2\text{Ti}_4\text{Pc}_5$. Compared with the spectra of the monomer, those of $\text{H}_2\text{Ti}_4\text{Pc}_5$ are shifted slightly to the red and broader. Excitonic interactions among mutually orthogonal chromophores are anticipated to be small.⁷ However, our calculations⁸ on the basis of an excitonic theory^{7a} predict Q band transitions for $\text{H}_2\text{Ti}_4\text{Pc}_5$ at 657, 689, 699 and 707 nm, and thus explain the broad and structureless Q band (the band at 689 nm corresponds to both in-plane and out-of-plane transitions and others are all in-plane transitions).

In conclusion, we have synthesized the first example of a well-defined mutually perpendicular phthalocyanine pentamer.

Notes and references

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- 5 The Ti=O stretching vibration, seen in the IR spectrum of TiOPc at 972 cm^{-1} , was absent in $\text{H}_2\text{Ti}_4\text{Pc}_5$.
- 6 Si_4Pc_4 was prepared by refluxing a toluene solution of tetra-*tert*-butylated SiPc in the presence of CaCl_2 and subsequent purification using gel-permeation columns of Bio-beads SX-1 (Bio-rad). It gave a parent ion peak at expected $m/z = 3142$ in the mass spectrum using MALDI-TOF technique, and satisfactory elemental analytical data.
- 7 (a) M. Kasha, H. R. Rawls and M. A. Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371; (b) The pseudo A term type Q band MCD spectra of the pentamer indeed suggests that the interaction of each constituting unit is not large M. J. Stillman and T. Nyokong, in *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, New York, 1989, Chapter 3.
- 8 N. Kobayashi and A. Muranaka, details will be published in a full paper. If the central Pc unit in $\text{H}_2\text{Ti}_4\text{Pc}_5$ contains TiO in its center, the Q transitions are anticipated at 689 (out-of plane), 683 and 711 (in-plane) nm.