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A novel fully conjugated phenanthroline-appended phthalocyanine: synthesis and characterisation

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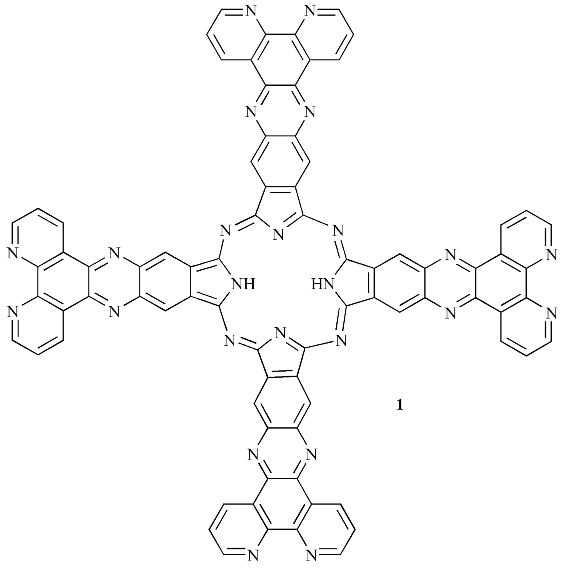
Received (in Cambridge, UK) 17th July 2002, Accepted 6th August 2002

The synthetic route to a new fully conjugated phenanthroline appended phthalocyanine is described. This compound has been fully characterised by elemental analysis, UV–VIS, IR, MS and ^{1}H NMR spectroscopy.

Phthalocyanines (Pcs) are a remarkably robust and versatile family of compounds of central importance for the industrial manufacture of blue and green pigments. They are however, currently finding new applications in a wide range of *high tech*. fields including non-linear optics, liquid crystals, Langmuir–Blodgett films, electrochromic devices, molecular metals, gas sensors, catalysts, photosensitisers, as well as therapeutic agents in pharmacology.[1] In light of their diverse repertoire of coordination chemistry, electronic properties, and stable core that is amenable to modification, Pcs can also be considered as useful building blocks for the construction of functional supramolecular assemblies. Along these lines, Pcs bearing peripheral lipophilic substituents displaying liquid-crystalline behaviour have been prepared.[2] Pcs containing macrocycles *e.g.* crown ethers or cryptands find potential applications as ion conducting channels or heavy metal extraction agents.[3] Pc derivatives with extended aromatic systems are showing potential as photosensitisers for the photodynamic therapy of cancer.[4] Furthermore, Pc derivatives with heteroaromatic substituents such as pyridine or terpyridine, covalently linked *via* a single σ-bond to the periphery of the macrocycle have also been reported with the aim of studying electron transfer processes.[5]

In recent years, there have been many attempts to construct organised artificial photosynthetic reaction centres comprised of a discrete number of assembled photoactive molecular subunits.[6] Pcs and their metal complexes have two strong absorption bands namely, in the far-red end (Q-band) and blue (B band) of the visible region.[1] The construction of multicomponent systems based on Pcs with other red chromophores may then convert a large part of the solar spectrum. While porphyrin-based multicomponent systems have been developed,[7] the attachment of a photo- or redox-active functionality directly onto Pc macrocycles has not been extensively explored. In order to address this situation we have recently focused our attention on the modification of the periphery of Pcs, with the aim of introducing additional ligands capable of coordinating metal ions. In this way, the coordination chemistry of the central cavity of the Pc, as well as the peripheral metal binding sites can be exploited for the assembly of new structural topologies with tunable optical, redox and electronic properties.

We report here, the synthesis and characterisation of the novel fully conjugated, tetrasubstituted H_2Pc **1**,[†] containing four peripheral diimine binding sites, fused *via* pyrazine bridges to a metal free phthalocyanine core. The synthetic route to this molecule is summarised in Scheme 1. The key intermediate in the synthesis is the precursor 4,4′-diaminophthalonitrile **5**. The starting material is 1,2-dibromo-4,5-dinitrobenzene **2** that is converted in the first step to 4-amino-1,2-dibromo-5-nitrobenzene **3**, by treatment with NH_3 in ethanol.[8a] The cyanide groups were then introduced *via* the Rosenmund–von Braun reaction,[8b] followed by reduction of the second nitro group to yield **5**.[8c] Condensation of **5** with 1,10-phenanthroline-5,6-dione in EtOH afforded the suitably functionalised phthalonitrile precursor **6**, as a pale yellow solid.[‡] Cyclotetramerisation of **6** in a refluxing solution of lithium metal dissolved in pentanol, followed by demetallation with acetic acid, afforded the crude, metal free H_2Pc **1** as a dark green solid.



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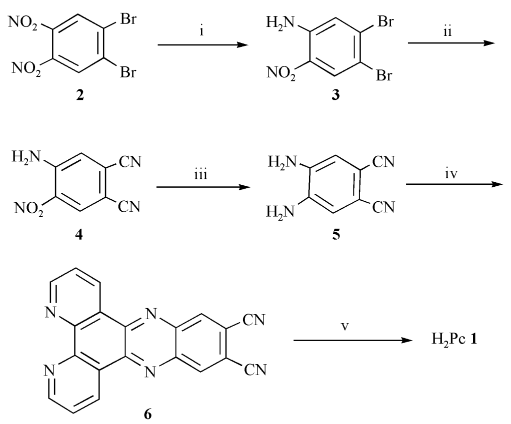
One of the major problems hindering the preparation, purification and characterisation of this compound is its insolubility in all common organic solvents. As a consequence, purification by chromatography or vacuum sublimation methods failed, and recrystallisation procedures were a challenge. Purification was finally achieved by repeatedly dissolving the H_2Pc in acetic acid followed by reprecipitation with acetone. This procedure was monitored by UV–VIS spectroscopy, since on removal of the impurities the Q-absorption band sharpened



Scheme 1 *Reagents and conditions*: (i) NH_3/EtOH (42%);[8a] (ii) CuCN, DMF/nitrobenzene, 180 °C, 4.5 h, (54%);[8b] (iii) $SnCl_2$, 70 °C, 20 min. (70%);[8c] (iv) 1,10-phenanthroline-5,6-dione, EtOH, reflux, 15 h (96%); (v) Li metal, Pent-OH, reflux, 24 h; then acetic acid (30%).

DOI: 10.1039/b206973c

slightly. The electronic absorption spectrum of this compound is dominated by two transitions, namely the higher-energy B band at 450 nm related to the Soret band of porphyrins (masked by absorptions from the peripheral diimine ligands), and the lower-energy, Q-band which in this case, actually stretches into the near infrared, for which a maximum is observed at 822 nm, Fig. 1. The broad shoulder at 750 nm can be assigned either to vibrational overtones of the Q-band,[9] or to a dimerisation of the Pc molecules in solution. The weaker absorption bands centred around 575 nm are more complex and are possibly due to π–π* transitions involving the fully conjugated electronic π-system of the Pc. The bathochromic shift of the Q-band can be attributed to two factors; firstly the extension of the aromatic π-system of the Pc which lowers the LUMO of the Pc macrocycle and shifts the Q-band further into the red and secondly, protonation of the basic nitrogens of the Pc in acidic media also serves to a shift the long wavelength maximum to longer wavelengths.[10] Comparsion of the IR data for compounds **1** and **6** clearly indicates the formation of the target compound by the disappearance of the C≡N str (2239 cm^{-1}) after Pc formation and the presence of NH stretching bands at 3402 and 1033 cm^{-1} due to the inner core of the macrocycle.† The C, H and N elemental analysis data for **1** are consistent with a Pc hydrate containing 18 molecules of water,† and in agreement with observations in the chemical literature that heterocyclic analogues of Pcs are often isolated as hydrates.[10] A reproducible peak at *m*/*z* = 1388 in the mass spectrum was observed, corresponding to the potassium salt of **1** plus a water molecule.† The ^1H NMR spectra for H_2Pc **1** and the phthalonitrile precursor **6** are shown in Fig. 2.‡ The aromatic protons (H_c and H_d), closest to the dinitrile groups are shifted upfield (0.12 ppm and 0.24 ppm, respectively) on formation of the Pc ring. Those protons further away from the reaction centre are, as expected, much less shifted on formation of the Pc. Since the spectrum was run in CF_3COOD, the inner NH protons are not visible. Due to poor solubility, we have not succeeded so far in obtaining reasonable ^{13}C NMR data for compounds **1** and **6**. The thermal properties of compound **1** were investigated by thermogravimetric analysis (TGA). Initial decomposition occurs at *ca.* 450–600 °C, most probably due to a loss of H_2O, and then extensive decomposition occurs at temperatures between 620–800 °C. The thermal stability of H_2Pc **1** is thus in agreement with aza-analogues of phthalocyanines which generally decompose without melting upon heating over 550 °C.[10] This may also account for our findings that this compound cannot be purified by sublimation, since this method is also reported to be unsuccessful for aza-analogues.[10]

To summarise, to the best of our knowledge, the first fully conjugated Pc containing four peripheral diimine binding sites has been prepared and obstacles hindering its purification and characterisation have been overcome. The central cavity of the macrocycle together with the peripheral binding sites present new exciting prospects for the linkage of a wide range of magnetic, electronic, redox and photo-active components. Indeed, the fully conjugated nature of this system should make it ideal for studying electron transfer processes. Further work in this direction is currently in progress.

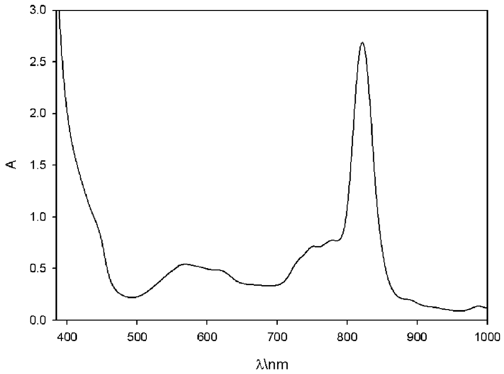


Fig. 1 UV–VIS spectra of **1** in trifluoroacetic acid.

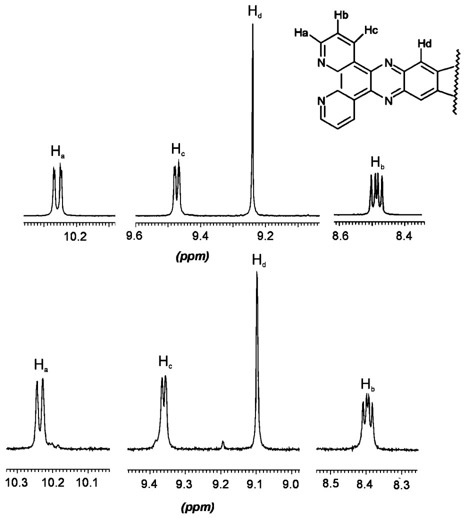


Fig. 2 ^1H NMR spectra (CF_3COOD) for compound **6** (top) and H_2Pc **1** (bottom). The labelling scheme is shown in the top right hand corner.

We wish to thank both Dr Eugen Stulz and Dr Shi-Xia Liu for their help and useful discussions.[11] This work was supported by the SNF programme on Supramolecular Chemistry.

Notes and references

† *Selected data for* **1**: anal. Calc. for $C_{80}H_{52}N_{24}O_{18}$: C, 58.00; H, 4.23; N, 20.30. Found C, 57.62; H, 3.91; N, 19.56 %; δ_H (500 MHz, CF_3COOD) 10.24 (d, 8H, *J* 4.68 Hz), 9.36 (d, 8H, *J* 3 Hz), 9.09 (s, 8H), 8.50 (dd, 8H, *J* 4.68, 3.00 Hz); IR (KBr disc): ν/cm^{-1} 3402, 1578, 1482, 1443, 1405, 1349, 1113, 1089, 1033, 887, 807, 739, 710, 623; UV-VIS (CF_3COOH): λ_{max}/nm 822, 750, 575, 450, 400; MS(MALDI) *m*/*z* 1388 $[C_{80}H_{36}N_{24}OK]H^+$ (K^+ is used for calibration purposes).

‡ *Selected data for* **6**: δ_H (500MHz, CF_3COOD): 10.26 (dd, 1H, *J* 6.21, 0.75 Hz), 9.47 (dd, 1H, *J* 4.68, 0.75 Hz), 9.23 (s, 1H), 8.50 (dd, 1H, *J* 6.21, 3.93 Hz); IR (KBr disc): ν/cm^{-1} 3373, 2240, 1607, 1581, 1509, 1405, 1359, 1242, 827, 726, 535; UV-VIS (CF_3COOH): λ_{max}/nm 310, 361, 381; MS (ESI) *m*/*z* 333 $[M]H^{\cdot+}$.

1 (*a*) *Phthalocyanines—Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Wiley, New York, vol. 1–4, 1989–1996; (*b*) N. B. McKeown, *Phthalocyanine Materials—Synthesis, Structure and Function*, Cambridge University Press, Cambridge, UK, 1998.
2 (*a*) K. Msayib, S. Makhseed and N. B. McKeown, *J. Mater. Chem.*, 2001, **11**, 2784; (*b*) A. S. Drager and D. F. O'Brien, *J. Org. Chem.*, 2000, **65**, 2257; (*c*) K. Petritsch, R. H. Friend, A. Lux, G. Rozenberg, S. C. Moratti and A. B. Holmes, *Synth. Met.*, 1999, **102**, 1776.
3 (*a*) C. F. van Nostrum, S. J. Picken, A.-J. Schouten and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1995, **117**, 9957; (*b*) Y. Gök, H. Kantekin, A. Bilgin, D. Mendil and I. Degirmencioglu, *Chem. Commun.*, 2001, 285; (*c*) B. Cabezón, E. Quesdada, S. Esperanza and T. Torres, *Eur. J. Org. Chem.*, 2000, 2767.
4 F. Mitzel, S. FitzGerald, A. Beeby and R. Faust, *Chem. Commun.*, 2001, 2596.
5 (*a*) M. Kimura, T. Hamakawa, T. Muto, K. Hanabusa and N. Kobayashi, *Tetrahedron Lett.*, 1998, **39**, 8471; (*b*) E. H. Morkved, H. Ossletten and H. Kjøsen, *J. Prakt. Chem.*, 2000, **342**, 83.
6 M. Kimura, T. Hamakawa, K. Hanabusa, H. Shirai and N. Kobayashi, *Inorg. Chem.*, 2001, **40**, 4775.
7 (*a*) D. Holten, D. F. Bocian and J. S. Lindsey, *Acc. Chem. Res.*, 2002, **35**, 57; (*b*) J. Li, J. R. Diers, J. Seth, S. I. Yang, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 9090; (*c*) A. Nakano, A. Osuka, I. Yamazaki, T. Yamasaki and Y. Nishimura, *Angew. Chem., Int. Ed.*, 1998, **37**, 3023.
8 (*a*) F. Schiff, *Monatsh.*, 1890, **11**, 338; (*b*) S. A. Mikhalenko, V. M. Derkacheva and E. A. Luk'yanets, *Russ. J. Gen. Chem.*, 1981, **51**, 1405; (*c*) E. V. Kudrik, G. P. Shaposhnikov and A. E. Balakirev, *Russ. J. Gen. Chem.*, 1999, **69**, 1321.
9 N. Kobayashi and A. Muranaka, *Chem. Commun.*, 2000, 1855.
10 S. V. Kudrevich and J. E. van Lier, *Coord. Chem. Rev.*, 1996, **156**, 163.
11 E. Stulz, C. C. Mak and J. K. M. Sanders, *J. Chem. Soc., Dalton Trans.*, 2001, 604.