

Structural characterisation of a red phthalocyanine

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Metal 1,4,8,11,15,18,22,25-octakis(hexylsulfanyl)phthalocyanines exhibit a weak absorption band in the 450–600 nm region, leading to novel dyes that include the red lead metallated derivative that has been characterised by X-ray crystallography.

Metallated phthalocyanines are commercially important blue/green dyes and pigments. Their intense colour arises from a strong and relatively narrow absorption band at *ca.* 700 nm (the Q-band) that arises from a π – π^* transition.¹ The energy of this transition shows some degree of sensitivity to the central metal ion. However, substituents, particularly when they are located at the non-peripheral (1,4,8,11,15,18,22,25) sites of the macrocycle, can show a much more marked effect leading to significant bathochromic shifts. Indeed, examples of near infra-red absorbing phthalocyanine dyes include derivatives bearing non-peripheral substituents linked through oxygen atoms (λ_{max} *ca.* 760 nm),² and sulfur (λ_{max} > 800 nm).³ However, there are no comparable structural modifications which shift the Q-band as significantly towards the blue.

In a programme designed to investigate phthalocyanine dye materials with colours other than blue or green, we have commenced investigation of the effect of substituents and metal centres on the energies of transitions other than the Q-band. These include the Soret, N, L and C transitions which normally occur in the UV spectrum.¹ Here we describe the novel 1,4,8,11,15,18,22,25-octakis(hexylsulfanyl)phthalocyanines **1–4** all of which exhibit a visible region transition between 450–600 nm.

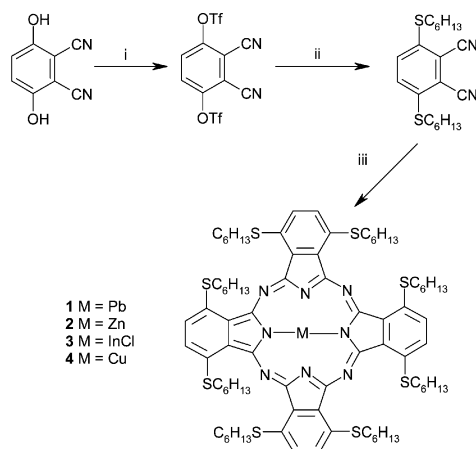
Compounds **1–4** were prepared in a convenient three step synthesis from dicyanohydroquinone according to Scheme 1.† Fig. 1 shows the UV to near-IR spectra for the four compounds. The series exhibits, as expected, the Q-band shifted into the near infra-red and the λ_{max} is clearly metal dependent. In contrast to the corresponding metallated 1,4,8,11,15,18,22,25-octaalkyl derivatives,⁴ the chloroindium derivative, **3**, shows the most

bathochromically shifted Q-band λ_{max} 836 nm, *cf.* **1**, λ_{max} 818 nm.†

Previous reports of arylsulfanyl substituted analogues³ focussed on the near-IR absorption band and gave no indication of visible region absorptions. Such absorptions clearly arise from the series **1–4**. The weak absorption just to the blue of the Q-band is a common feature of phthalocyanine electronic absorptions and can be assigned to a transition to a higher vibrational level. However, there is also a weak, broad band in the 450–600 nm region, Fig. 1 (inset). The energies of these two weak bands are sensitive to the metal centre and give rise to the variation in the colours of the four phthalocyanine derivatives. Thus in the solution phase the zinc derivative **2** is brown, the chloroindium derivative **3** mauve and the copper derivative **4** purple. The lead derivative **1** proves to be a red dye, crystallising as deep red needle-prisms, mp 144–146 °C, from THF–acetone and dissolving in various organic solvents to form red solutions.

A burnished film of **1**, *i.e.* one formed by smearing crystals onto a glass slide, shows a Q-band at 859 nm. This compares with λ_{max} 818 nm in the solution phase. The shift to longer wavelength in the solid state implies a packing dissimilar from, for example, the columnar packing of the ‘shuttlecock’ shaped molecules of unsubstituted lead phthalocyanine in its monoclinic form.⁵ X-Ray crystallography of **1** confirmed this. The room-temperature X-ray structure analysis shows a single, unique molecule in a triclinic cell; pairs of these molecules lie about centres of symmetry. The cores of the molecules, *i.e.* Pb, the eight N and the thirty-two sp^2 C atoms, are well-resolved and they refined satisfactorily. However, gross disorder was found in four of the eight hexyl groups, and the refinement was concluded with rather high *R*-values, *viz.* $wR_2 = 0.271$ and $R_1 = 0.196$ for all 12005 reflections; for the 5082 observed reflections, $R_1 = 0.094$.

To improve the resolution, intensity data were measured at 140 K. The cell is now twice as large and there are two independent molecules in the asymmetric unit, *i.e.* four in the triclinic cell with $P\bar{1}$ symmetry.‡ The two molecules, denoted as



Scheme 1 Reagents and conditions: i) Triflic anhydride, 2,6-lutidine, CH_2Cl_2 , -20 °C to RT, 65%. ii) Hexanethiol, K_2CO_3 , DMSO, RT, 70%. iii) $\text{M}(\text{OAc})_2$ or InCl_3 , DBU, PeOH , reflux, 15–55% depending upon M.

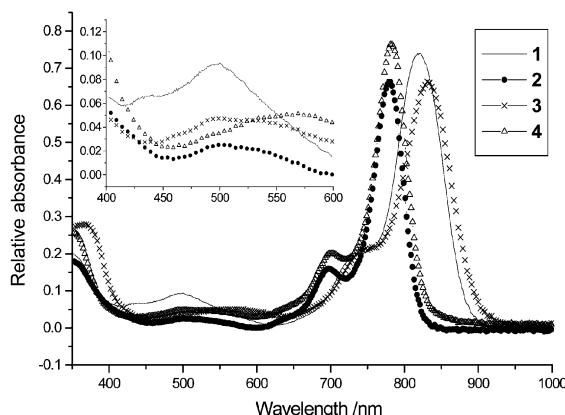


Fig. 1 Absorption spectra of compounds **1–4** in THF between 350–1000 nm and, inset, expansion of 400–600 nm region.

1A and **1B**, are very similar in dimensions, orientation and in the arrangements of the hexyl side-chains (Table 1 and Fig. 2). The two lead atoms Pb(1) and Pb(2) in **1A** and **1B** respectively are each four-coordinate, and lie 1.339(4) and 1.306(4) Å out of the square planes of four nitrogen atoms; mean Pb–N distances are 2.406(10) and 2.391(8) Å in the two molecules.

There are significant differences in the tilt of the benzenoid ring groups which define the saddle-shape patterns of the cores of the molecules. The angles between the normals of opposite benzenoid groups in molecule **1A** are 19.0(4) and 24.1(4)°, whereas the corresponding angles in molecule **1B** are 13.9(4) and 14.4(4)°. The hexyl side-chains are much better resolved at low temperature, but two chains in each molecule still show disorder, with alternative sites for some of the carbon atoms in the chain. All eight of the hexylsulfanyl groups in each molecule lie approximately in the plane of the core of that molecule. The hexyl groups on the sulfur atoms S(7), S(17), S(27) and S(37) are all well-resolved and have all-*trans* conformations; the carbon atoms all lie close to the core plane with their hydrogen atoms directed out of that plane. Of the other hexyl groups, those on S(14) and S(24) show disorder; those on S(34) are ordered but show two *gauche* links in the chain. The conformations of the S(4) hexyl groups show the major difference between the two molecules **1A** and **1B**. In **1A**, the hexyl chain is all-*trans*, whereas in **1B**, there are *gauche* conformations about S(4)–C(41) and C(42)–C(43). In all cases, the pairs of hexyl groups on adjacent S atoms, e.g. those on S(7) and S(14), lie approximately parallel.

Table 1 Selected molecular dimensions in complex **1**. Bond lengths are in Å, angles in degrees. E.s.d.s are in parentheses

	Molecule 1A with Pb(1)	Molecule 1B with Pb(2)
Pb(n)–N(1)	2.409(7)	2.370(7)
Pb(n)–N(11)	2.427(8)	2.411(9)
Pb(n)–N(21)	2.380(9)	2.392(9)
Pb(n)–N(31)	2.406(7)	2.393(8)
N(1)–Pb(n)–N(11)	72.2(3)	72.7(3)
N(21)–Pb(n)–N(1)	112.5(3)	113.9(3)
N(31)–Pb(n)–N(1)	71.5(3)	72.8(3)
N(21)–Pb(n)–N(11)	71.7(3)	72.2(3)
N(31)–Pb(n)–N(11)	112.2(3)	113.8(3)
N(21)–Pb(n)–N(31)	72.4(3)	72.9(3)
Mean Pb–N	2.406(10)	2.391(8)
Mean N–Pb–N(cis)	71.9(2)	72.7(2)
Mean N–Pb–N(trans)	112.3(2)	113.85(5)
Displacement of Pb from N ₄ plane	1.339(4)	1.306(4)
Angles between opposite C ₆ rings	19.0(4)	13.9(4)
	24.1(4)	14.4(4)

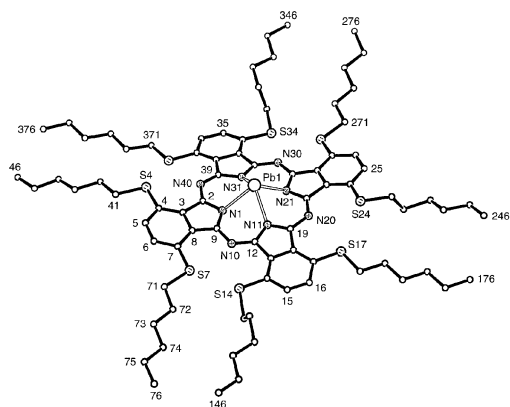


Fig. 2 View of molecule **1A**, with Pb(1) in its core. Hydrogen atoms, and the disorder in two of the hexyl chains, have been omitted for clarity. Differences between **1A** and **1B** are outlined in the text.

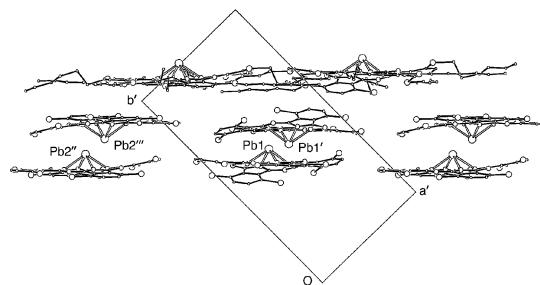


Fig. 3 Packing of molecules in crystals of **1** viewed down the *c* axis. Molecules lie in sheets, as in the top layer of the diagram; the lower two layers show pairs of Pb-phthalocyanine cores about centres of symmetry, e.g. **1A** and **1A'** about $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and **1B'** and **1B''** about $(-\frac{1}{2}, 1, 0)$. The minor differences in the projections of the **1A** and **1B** molecules may be discerned.

The overall packing arrangements (Fig. 3) show pairs of molecules linked about centres of symmetry with short distances between the molecules, viz. the Pb...N(30'), ...S(27') and ...S(34') distances are 3.292(8), 3.371(3) and 3.484(3) Å between the **1A** and **1A'** molecules, correspondingly 3.254(8), 3.444(4) and 3.448(3) Å between pairs of **1B** molecules. The pairs of molecules are stacked parallel to the *a* axis in the crystal, with the **1A** molecules forming stacks about *y* = 0.5 and the **1B** molecules about *y* = 0.0 and 1.0.

In summary, we have identified a series of differently coloured metallated phthalocyanines having non Q-band absorptions in the 450–600 nm region. The lead derivative is red and has been characterised by X-ray crystallography.

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Notes and references

† *Selected data*: **1** λ_{max} (THF) 818 nm. Anal. found C, 58.29; H, 6.65; N, 6.65; C₈₀H₁₁₂N₈S₈Pb requires C, 58.25; H, 6.84 and N, 6.79. **2** λ_{max} (THF) 781 nm. Anal. found C, 63.84; H, 7.43; N, 7.37; C₈₀H₁₁₂N₈S₈Zn requires C, 63.73; H, 7.49 and N, 7.43. **3** λ_{max} (THF) 836 nm. Anal. found C, 60.66; H, 7.11; N, 6.84; C₈₀H₁₁₂N₈S₈InCl requires C, 60.33; H, 7.09 and N, 7.04. **4** λ_{max} (THF) 783 nm. Anal. found C, 63.39; H, 7.53; N, 7.31; C₈₀H₁₁₂N₈S₈Cu requires C, 63.73; H, 7.48 and N, 7.43.

‡ *Crystal data*: C₈₀H₁₁₂N₈PbS₈, *M* = 1649.4. Triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 11.252(1), *b* = 22.306(8), *c* = 31.546(6) Å, α = 93.41(3), β = 91.73(1), γ = 90.84(1)°, *V* = 7899(3) Å³, *Z* = 4, *D_c* = 1.387 g cm⁻³, *F*(000) = 3432, *T* = 140(1) K, μ (Mo–K α) = 24.0 cm⁻¹, λ (Mo–K α) = 0.71069 Å. Intensity data recorded on a Rigaku R-Axis IIC image plate diffractometer equipped with a rotating anode X-ray source and graphite monochromator. Total no. of reflections recorded, to θ_{max} = 25.5°, was 24489 with 16497 unique (*R*_{int} = 0.073); 9571 'observed' with *I* > 2 σ . The non-hydrogen atoms, except in the disordered parts of the side-chains and for three atoms which went "non-positive-definite", refined with anisotropic thermal parameters. Hydrogen atoms included in idealised positions (except in the disordered areas) and their *U*_{iso} values set to ride on the *U*_{eq} values of the parent carbon atoms. Final *R*-factors: *wR*₂ = 0.145 and *R*₁ = 0.110 for all 16497 reflections weighted $w = [\sigma^2(F_o^2) + (0.0648P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for 'observed' data only, *R*₁ = 0.055. Final difference peaks (to ca. 0.75 e Å⁻³) close to the Pb atoms. CCDC 208895. See <http://www.rsc.org/suppdata/cc/b3/b304173p/> for crystallographic data in .cif format.

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