

# Synthesis, structure and optical characterisation of silicon phthalocyanine bis-esters

2 PERKIN

Christopher Farren, Simon FitzGerald, Martin R. Bryce,\* Andrew Beeby\* and Andrei S. Batsanov

Chemistry Department, University of Durham, South Road, Durham, UK DH1 3LE.

E-mail: m.r.bryce@durham.ac.uk, andrew.beeby@durham.ac.uk

Received (in Cambridge, UK) 26th September 2001, Accepted 31st October 2001

First published as an Advance Article on the web 3rd December 2001

A range of axially substituted silicon phthalocyanines has been synthesised using various carboxylates as the ligands. 4-*tert*-Butylbenzoic acid gives rigid, orthogonal axial substituents, whilst a thiophene-containing bis-acetate was conformationally more flexible. Varying the aromatic substituents of phenylacetic acids gave phthalocyanines with altered spectroscopic properties, and changes in the alkyl chain length between the phthalocyanine and the aromatic nucleus of the ligand induced variations in the fluorescence lifetime and quantum yield. Three X-ray crystal structures of axially substituted silicon phthalocyanine bis-esters have been determined.

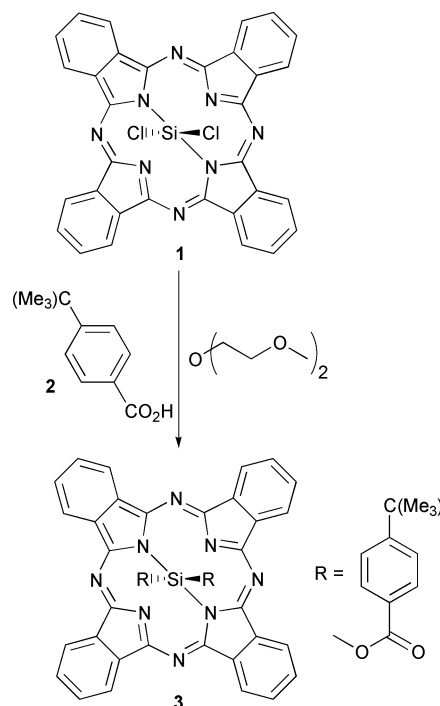
## Introduction

Phthalocyanines (pcs) and related macrocycles comprise a robust and versatile class of compounds,<sup>1</sup> and continue to attract considerable attention due to their characteristic optical and coordination properties.<sup>2</sup> Interest currently lies in the preparation of structurally modified pc systems, with the subsequent potential applications including medicinal therapeutic agents,<sup>3</sup> electrochromic<sup>4</sup> and non-linear optical devices,<sup>5</sup> catalysts,<sup>6</sup> electro-catalysts,<sup>7</sup> liquid crystalline materials,<sup>8</sup> photosensitisers<sup>9</sup> and photoconductors.<sup>10</sup> Both binuclear<sup>11</sup> and heteroatom-containing species<sup>12</sup> have been described, and pcs with either chemically, electrically or biologically 'active' *peripheral* groups such as fullerenes,<sup>13</sup> ferrocenes,<sup>14</sup> crown ethers,<sup>15</sup> bi- and tri-pyridyls,<sup>16</sup> tetrathiafulvalenes,<sup>17</sup> dendrimers,<sup>18</sup> sugars,<sup>19</sup> nucleobases<sup>20</sup> and amino acids<sup>21</sup> are currently under investigation. In contrast to this vast array of functionality, there are relatively few *axially* substituted silicon pcs,<sup>22</sup> despite the fact that such species have higher quantum yields and longer fluorescence lifetimes than the more common zinc or aluminium pcs<sup>1b</sup> and are thus more suited to optical studies. Furthermore, axially substituted pcs are not able to aggregate in solution, giving rise to sharp UV-Vis absorption peaks.<sup>23</sup> Our current interests lie in the preparation of novel, silicon pc derivatives in which the optical properties of the macrocyclic core are modified by the axial ligands. However, while examples of silicon pc bis-*ethers* have been reported, using various simple<sup>24</sup> or dendritic<sup>25</sup> alcohols as the axial ligands, alternate linker groups are more rarely described and yet may provide a wider range of functionalised systems. Indeed, reports of silicon phthalocyanine bis-esters are currently extremely scarce.

## Synthesis

We first elected to synthesise a reference pc compound for the UV-Vis spectroscopic investigation, ideally with high solubility and minimal electronic or steric interaction between the axial ligands and the macrocyclic core. Thus silicon phthalocyanine dichloride **1** was reacted with 4-*tert*-butylbenzoic acid **2** in a polyether solvent at 160 °C to give *axially* substituted silicon phthalocyanine bis(4-*tert*-butyl)benzoate **3** as a dark blue solid in 39% yield after column chromatography (Scheme 1).

Having an appropriate reference compound allows quantita-



Scheme 1 General reaction scheme.

tive investigations of more functionalised species. Recently, pcs substituted with *peripheral* thiophene units have been described<sup>26</sup> and we now report that silicon phthalocyanine dichloride **1** reacts with thiophene-3-acetic acid **4** as described above to give *axially* substituted silicon phthalocyanine bis-(3-thienyl)acetate **5** in 35% yield, again as a dark blue solid. Subsequently, in light of the optical effects (reported below) displayed by these two compounds, we synthesised a range of silicon phthalocyanine bis-acetates with relatively electron rich axial ligands, as in Table 1. Having determined that in some cases the flexibility of the methylene group allows a degree of interaction between the ligand functional group and the pc core, it was decided to specifically examine this phenomenon with respect to linker group length. Hence, a series of dimethoxyphenyl acids were reacted with **1** (Table 2).

**Table 1** Synthesis of substituted silicon phthalocyanine bis-esters

Starting acid	Product	Yield (%)
4- <i>tert</i> -Butylbenzoic acid <b>2</b>	Silicon phthalocyanine bis-(4- <i>tert</i> -butyl)benzoate <b>3</b>	39
Thiophene-3-acetic acid <b>4</b>	Silicon phthalocyanine bis-(3-thienyl)acetate <b>5</b>	35
(2-Methoxyphenyl)acetic acid <b>6</b>	Silicon phthalocyanine bis-(2-methoxyphenyl)acetate <b>7</b>	24
(3-Methoxyphenyl)acetic acid <b>8</b>	Silicon phthalocyanine bis-(3-methoxyphenyl)acetate <b>9</b>	21
(4-Methoxyphenyl)acetic acid <b>10</b>	Silicon phthalocyanine bis-(4-methoxyphenyl)acetate <b>11</b> <sup>a</sup>	17
(2,5-Dimethoxyphenyl)acetic acid <b>12</b>	Silicon phthalocyanine bis-(2,5-dimethoxyphenyl)acetate <b>13</b>	35
(3,4-Dimethoxyphenyl)acetic acid <b>14</b>	Silicon phthalocyanine bis-(3,4-dimethoxyphenyl)acetate <b>15</b>	28
(3,4,5-Trimethoxyphenyl)acetic acid <b>16</b>	Silicon phthalocyanine bis-(3,4,5-trimethoxyphenyl)acetate <b>17</b> <sup>b</sup>	25

<sup>a</sup> Product is sufficiently insoluble to prevent good <sup>13</sup>C NMR characterisation. <sup>b</sup> Product is slightly unstable and decomposes upon storage.

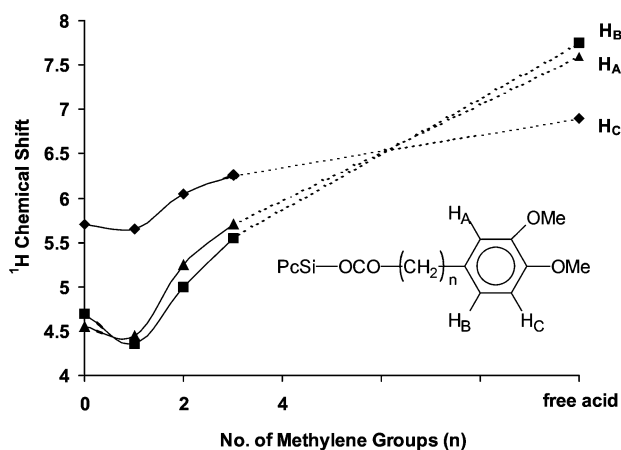
**Table 2** Synthesis of silicon phthalocyanine bis-esters of varying linker length

Starting acid	Product	Yield (%)
3,4-Dimethoxybenzoic acid <b>18</b>	Silicon phthalocyanine bis-(3,4-dimethoxy)benzoate <b>19</b> <sup>a</sup>	34
(3,4-Dimethoxyphenyl)acetic acid <b>14</b>	Silicon phthalocyanine bis-(3,4-dimethoxyphenyl)acetate <b>15</b>	28
3-(3,4-Dimethoxyphenyl)propanoic acid <b>20</b>	Silicon phthalocyanine bis-3-(3,4-dimethoxyphenyl)propanoate <b>21</b>	38
4-(3,4-Dimethoxyphenyl)butanoic acid <b>22</b>	Silicon phthalocyanine bis-4-(3,4-dimethoxyphenyl)butanoate <b>23</b> <sup>b</sup>	25

<sup>a</sup> Product is sufficiently insoluble to prevent good <sup>13</sup>C NMR characterisation. <sup>b</sup> Product is slightly unstable and decomposes upon storage.

Compound **3** had high solubility in common organic solvents, and was stable for at least 12 months in the solid form under ambient conditions. Samples of **3** dissolved in an aerated mixture of THF and water (10 : 1 v/v) were stable in the dark over a period of weeks, and were only slowly decomposed over a period of days when irradiated with sunlight (as measured by the decay of the sharp transition in the UV/Vis spectrum). In addition, axially substituted pcs have very characteristic <sup>1</sup>H NMR spectra, as the close proximity of the ligand to the large pc ring current induces a large upfield shift (*i.e.* to low frequency) in the proton NMR resonances.<sup>27</sup> The four aromatic hydrogen atoms of **3** thus give two distinct doublets at 5.07 and 6.25 ppm respectively, compared to 7.50 and 8.06 ppm for the free acid, and the pc equatorial protons give downfield-shifted resonances as unresolved multiplets observed at 8.38 and 9.71 ppm. Electrospray mass spectroscopy showed the expected isotope distribution pattern for both the molecular ion and the [M + Na]<sup>+</sup> and [M + K]<sup>+</sup> ions, and accurate mass measurements on the large [M + Na]<sup>+</sup> ion gave the expected molecular formula to within acceptable limits. In addition, crystals of the bis-ester were obtained by slow diffusion of hexane into a solution of **3** in DCM, and X-ray crystallographic studies (reported in detail below) confirmed the molecular arrangement.

Characterisation of **5** proceeded similarly to that of the reference compound **3**, with the ligand methylene protons giving a singlet at 0.65 ppm in the <sup>1</sup>H NMR spectrum and the aromatic thiophene hydrogen atoms giving three distinct resonances between 4.41 and 6.06 ppm. Indeed, most of the product bis-esters are stable, blue solids under ambient conditions, and can be characterised as above using standard analytical techniques. Notably, as the symmetry of the molecule increases the solubility decreases, so while **7** is very soluble in common organic solvents **11** is relatively insoluble, and good <sup>13</sup>C NMR spectra cannot be obtained. Unfortunately, the higher rigidity of the bis-benzoate **19** also resulted in reduced solubility, and the bis-butanoate **23** decomposed upon storage, implying that the ester linkage is increasingly susceptible to hydrolysis when sterically more accessible. Crystals of **5** and **21** suitable for X-ray analysis were obtained as above, and are discussed in detail below. Interestingly, as the chain length between pc and ligand aromatic moiety increases the <sup>1</sup>H NMR chemical shifts of the three dimethoxybenzene aromatic protons vary in turn, giving a qualitative measure of the ring current that the axial ligand is experiencing (Fig. 1). The final data points on the graph are

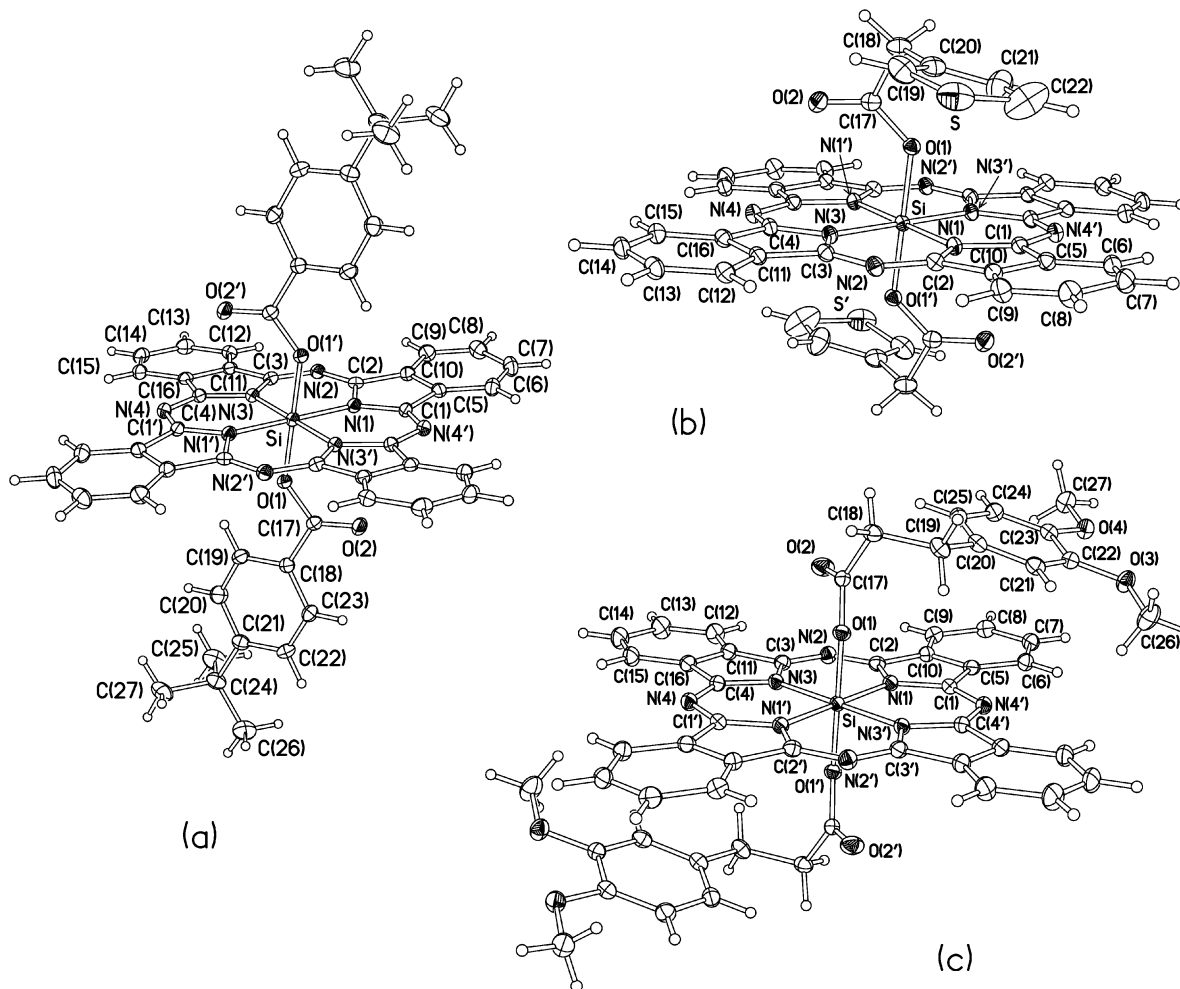


**Fig. 1** Variation of ligand <sup>1</sup>H chemical shift with spacer length.

those of the free acid, *i.e.* experiencing no external electronic effects.

### X-Ray crystallographic studies

Molecular structures of **3**, **5** and **21** are similar (Fig. 2) in that for each case the Si atom lies at a crystallographic inversion centre and has an octahedral coordination, distorted by compression along the O...O axis. Si–N bond distances are similar to those in other (pc)Si(OR)<sub>2</sub> compounds,<sup>28</sup> but *ca.* 0.05 Å shorter than in (pc)Si.<sup>29</sup> The pc ligand is planar with a slight twisting distortion. The average deviation of the 41 atoms from their mean plane is 0.05 (**3**), 0.06 (**5**), 0.03 Å (**21**), and the maximum deviation is 0.11, 0.14 and 0.07 Å, respectively. In all three molecules, the COO group is nearly normal to the pc plane with dihedral angles of 88° in **3**, 73° in **5** and **21**. In **3** the twist between the benzene and carboxy group planes is small (11°), hence the benzene ring is inclined to the pc plane by 84°. In **5**, the methylene spacer allows more flexibility: the essentially planar thiophene ring is inclined by 71° to the carboxy group plane and by 12° to the pc plane. A similar conformation is adopted by molecule **21**, with two methylene spacers: the benzene–carboxy and benzene–pc angles are 85° and 16°, respectively. An analogous self-stacking mode has been observed in complexes (pc)Si(OR)<sub>2</sub>, where R is substituted



**Fig. 2** Molecular structures of **3** (a), **5** (b) and **21** (c), showing 50% thermal ellipsoids. Primed atoms are symmetrically dependent *via* inversion centres. Selected bond distances (Å): Si–N(1) 1.914(2), 1.906(1), 1.904(1); Si–N(3) 1.909(2), 1.912(1), 1.913(1); Si–O(1) 1.754(1), 1.762(1), 1.756(1) (in **3**, **5** and **21** respectively). The thiophene rings in **5** are disordered over two orientations, only the major thiophene conformer is shown.

pyridine<sup>28a</sup> (dihedral angle 16°) or ferrocenyl<sup>28b</sup> (dihedral angle *ca.* 7°).

Structure **3** contains infinite stair-like stacks of pc moieties (Fig. 3a). Each two adjacent molecules are related *via* translation *c* and overlap by pairs of (*cis*) pc benzene rings. The interplanar separation between the latter (3.38 Å) and the shortest C···C contacts (3.30–3.37 Å) indicate a close stacking of aromatic rings. A similar pc-stacking motif (Fig. 3b) exists in **5** (interplanar separation 3.42 Å, shortest C···C contacts 3.34–3.39 Å), but there the stacking involves thiophene rings as well (Fig. 4a): stacks of pc are interspersed with layers of thiophenes. In the structure of **21** the overlap of pc-moieties, related by the *a* translation, is only marginal (Fig. 3c) and the interplanar separation is wider (3.50 Å). Here stacks of pc are separated by double layers of axial substituents (Fig. 4b). In both **3** and **5** the pc-planes of molecules belonging to different stacks are not parallel but contact in a herringbone pattern, whereas in the triclinic crystal of **21**, all pc moieties are parallel and the packing can be described as laminar.

### Absorption and fluorescence spectroscopy

Reference compound **3** shows typical monomeric absorption (Table 3 and Fig. 5) in the concentration range 10<sup>−4</sup>–10<sup>−7</sup> M with an  $\epsilon_{\max}$  value of 2.9 × 10<sup>5</sup> dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>, this high value resulting from the very sharp electronic transitions seen with silicon phthalocyanines, and agreeing well with literature values.<sup>30</sup> The retention of monomeric behaviour even in 10<sup>−4</sup> M solution shows the effectiveness of the axial substituents in pre-

**Table 3** Spectroscopic data

Compound	$\lambda_{\max}$ (abs)/nm	$\lambda_{\max}$ (em)/nm	$\phi_f^a$	$\tau_f/\text{ns}^b$
<b>3</b>	685	691	0.62	6.7
<b>5</b>	685	691	0.39	6.7
<b>7</b>	685	693	0.66	6.8
<b>9</b>	685	693	0.64	6.8
<b>11</b>	686	694	0.64	6.8
<b>19</b>	688	693	0.64	6.5
<b>15</b>	687	694	0.57	6.4
<b>21</b>	685	693	0.50	5.6
<b>23</b>	686	693	0.57	6.2
<b>13</b>	687	694	0.08	0.96 <sup>c</sup>
<b>17</b>	686	696	0.33	3.8 <sup>d</sup>

<sup>a</sup>  $\pm$  10%. <sup>b</sup>  $\pm$  0.1 ns. <sup>c</sup> A second, minor component was also detected: 5.1 ns (5%). <sup>d</sup> A second, minor component was also detected: 2.4 ns (9%).

venting the macrocycles from undergoing intermolecular interactions. Like other silicon pcs reported in the literature, the quantum yield and fluorescence lifetime values are both high, almost double those values obtained for the more common zinc pcs.<sup>1b</sup> The rigid axial ligand efficiently isolates the chromophoric pc ring and hence **3** acts as a very useful and robust reference compound with which the other compounds described in this paper may be compared.

Compound **5**, with the electron rich thiophene group, shows similar behaviour to **3** in all but the fluorescence quantum yield, which is some 40% lower than that of **3**. This may be a consequence of the large electron density present on the thiophene

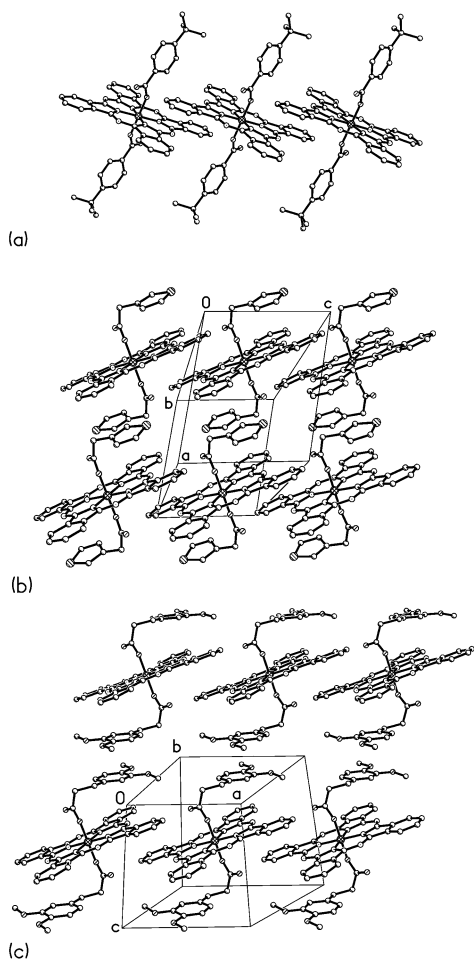


Fig. 3 Pc stacking in the crystal packing of **3** (a), **5** (b) and **21** (c).

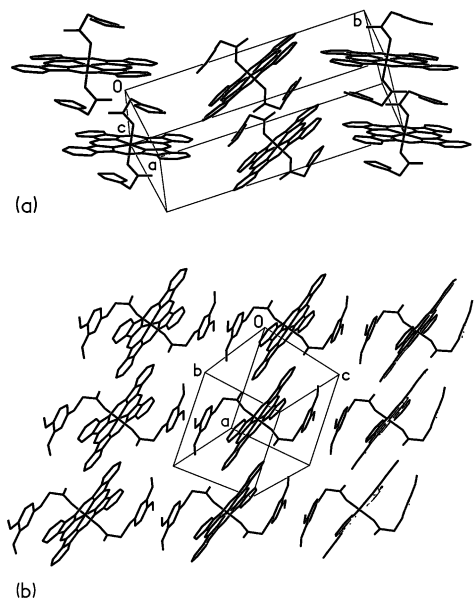


Fig. 4 Pc stacking in the crystal packing of **5** (a) and **21** (b), viewed parallel to the pc plane.

ring; combined with the added flexibility that the acetic acid linker affords, the possibility of fluorescence quenching by electron transfer is realised. Indeed, pcs have long been known to undergo electron transfer reactions, both to and from their excited states, that is, acting as both oxidising and reducing species. Electron *acceptors* such as methyl viologen have been shown to quench the pc *singlet* excited state,<sup>31</sup> whilst some

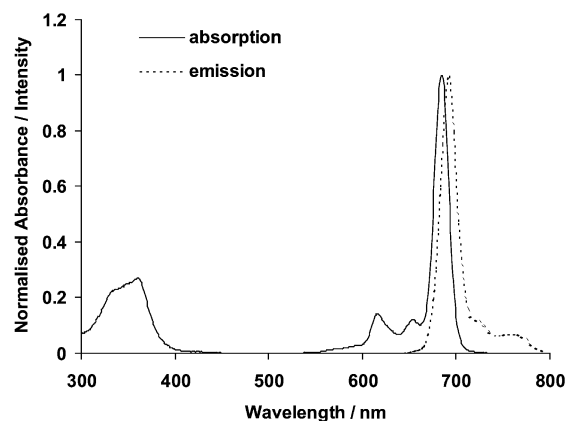


Fig. 5 Absorption and fluorescence spectra of **3**.

organic oxidants also quench the *triplet* state.<sup>32</sup> Electron *donors* also quench phthalocyanine excited states, including tetrathiafulvalene derivatives<sup>17b</sup> and functionalised amines.<sup>33</sup>

Strangely, the fluorescence lifetime of **5** is unperturbed, a phenomenon which has been observed with similar species currently under study in our laboratories, and the calculated rate constant of fluorescence,  $k_f$  ( $5.3 \pm 0.5 \times 10^7 \text{ s}^{-1}$ ), is significantly lower compared with that for **3** and the other phthalocyanines studied here ( $9.2 \pm 0.5 \times 10^7 \text{ s}^{-1}$ ). It is suggested that there are two possible states for this compound—an “on” state in which fluorescence is observed with a normal lifetime of 6.7 ns, and an “off” state in which fluorescence is rapidly and efficiently quenched, and for which the lifetime is very short. However, no quenching of reference compound **3** by the addition of thiophene-3-acetic acid **4** was observed in DCM even at a quencher concentration of 0.1 M, indicating that  $k_Q < 3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the intermolecular quenching process.

In order to confirm the hypothesis that the electron rich axial ligand in **5** induces electron transfer quenching, the 2-, 3- and 4-methoxy substituted phenylacetic acid derivatives **7**, **9** and **11** were synthesised. Lifetimes of 6.8 ns were recorded for all three, and quantum yields matching that of **3** make it quite clear that the excited state is unperturbed by the axial substituents. Hence, apart from some additional absorption below 300 nm corresponding to the methoxybenzene moiety these compounds are spectroscopically identical to **3**. Taking this process one step further produced the 3,4-dimethoxyphenylacetic acid substituted species **15**, and a small decrease in quantum yield and lifetime suggests a degree of quenching by the increasingly electron rich ligands. The tunability of this quenching with varying ligand arm length was investigated by synthesising the 3,4-dimethoxy substituted derivatives **19**, **21** and **23**, with 0, 2 and 3 methylene unit spacers respectively (Table 2). **19** shows comparable behaviour with **3**, followed by a small decrease in both lifetime and quantum yield for **15**, which suggests a small increase in quenching of the excited state, while **21** shows a reduction of almost 20% in both lifetime and quantum yield compared with the reference compound **3**. In contrast, **23**, with the longest chain, is somewhat more fluorescent than **21** whilst still displaying reduced emission relative to **3**. This behaviour may result from two opposing effects, the first of which relates to the flexibility of the ligand chain. As seen in the crystal structure of **3** (Fig. 3a) an axial ligand with no degree of flexibility holds the aryl group perpendicular to the phthalocyanine ring, and as the ligand experiences increased freedom of movement the aryl group can achieve closer proximity to the phthalocyanine ring (Fig. 3b, 3c). However, as the ligand arm is elongated by additional methylene units the aromatic ring becomes more distant from the phthalocyanine, and this reduction in interaction directly opposes the effect of increased flexibility. Hence a small increase in quenching is initially observed,

**Table 4** Rehm–Weller calculations

Quenching unit	$E_{\text{ox}}/\text{V}^a$	$\Delta G/\text{kJ mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$k_{\text{Q}}/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (calc.) <sup>b</sup>	$\phi_{\text{f}}$ (exp.) <sup>c</sup>
4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CO <sub>2</sub> H	+1.93	33.2	35.9	$2.5 \times 10^4$	0.64
3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H	+1.63	4.2	12.3	$4.3 \times 10^8$	0.57
3,4,5-(MeO) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H	+1.58	-0.62	9.7	$1.2 \times 10^9$	0.33
2,5-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H	+1.54	-4.4	8.0	$2.2 \times 10^9$	0.08

<sup>a</sup> vs. NHE. <sup>b</sup> Rate constant for quenching of phthalocyanine by quenching unit. <sup>c</sup> Phthalocyanine fluorescence quantum yield,  $\lambda_{\text{ex}} = 612 \text{ nm}$ .

and at this point the relative gain in flexibility just outweighs the increase in chain length, allowing the quenching unit to lie closer to the chromophore. For **23**, with three methylene units, the data indicate that quenching is less significant, presumably because the quencher unit is now too far removed from the phthalocyanine, despite the increased flexibility. Indeed, molecular modelling of these systems using the program CAChe clearly shows that as the number of methylene units is increased from 0 to 3 the axial ligand becomes increasingly flexible, sufficiently so to allow the quencher unit into close proximity with the phthalocyanine chromophore. However, the optimised structure for **23**, with 3 methylene units, shows the quenching unit to be only partially overlapping with the phthalocyanine ring, such is the length of the axial arm.

It is of interest that significant quenching was observed for the related dimethoxy-substituted compound, **13**, with a greater than 85% decrease in both fluorescence lifetime and quantum yield. **13** is isomeric with **15**, differing only in the substitution pattern of the two methoxy groups on the axial substituent, and yet behaves remarkably differently. The 2-, 3- and 4-methoxy substituted species **7**, **9** and **11** show that simply altering the position of the methoxy group relative to the chain attachment point has no effect upon the quenching, but what is important in **13** is the presence of the 1,4-dimethoxy arrangement, whereby a resonance canonical with a quinoidal structure can exist. This lowers the oxidation potential of the aryl moiety (+1.54 V for **13** vs. +1.63 V for **15**, see Experimental section for full details) and hence electron transfer to the phthalocyanine becomes more favourable.

Calculations according to the theory of Rehm–Weller<sup>34</sup> (Table 4) allow a quantitative estimation of  $k_{\text{Q}}$ , the rate constant for fluorescence quenching by electron transfer. Using solvent parameters for dichloromethane, a value of  $E(\text{Pc}/\text{Pc}^-) = -0.69 \text{ V}$ , a pc excited state energy of  $\Delta E_{\text{pc}}(0,0) = 1.81 \text{ eV}$  and  $E(\text{Q}^+/\text{Q})$  values for the quencher units, calculated values for  $k_{\text{Q}}$  can be obtained which relate directly to the oxidation potential of the methoxy substituted species. Despite the small difference in oxidation potential for the 1,2- and 1,4-dimethoxybenzene systems, there is a calculated five-fold increase in  $k_{\text{Q}}$  for the 1,4-substituted compound. Our experimental results concur qualitatively, with **13** showing a ten-fold increase in quenching, relative to **15**. Furthermore, the mono-substituted species are predicted to have rate constants  $10^5$  times smaller than that of the 1,4-substituted **13**, and our experiment shows no observable quenching. A compound with intermediate oxidation potential of +1.58 V, the 1,2,3-trimethoxy substituted **17**, shows a corresponding quantum yield of 0.33, 47% quenched relative to the unquenched mono-substituted **7**, **9** and **11**. In all cases, no *intermolecular* quenching between the ligand and **3** was observed at quencher concentrations up to 0.1 M, that is,  $k_{\text{Q}} < 3 \times 10^8 \text{ M}$ , which is in agreement with the calculated values for such a process.

## Conclusions

We have synthesised a range of new silicon pc derivatives with axial ester substituents, most of which are stable at ambient conditions and are highly soluble in a range of common organic solvents. X-ray studies have illustrated how such axially substituted pc systems pack, with the flexibility of the ligand

having a significant effect. The axial ligands efficiently prevent aggregation of the pc chromophores, as evidenced by the very sharp transition in the visible spectrum. The luminescence properties of these species have been investigated, and show long lifetimes and large quantum yields typical of silicon phthalocyanines. Efficient quenching of the pc emission has been observed in the presence of electron donating ligands. The degree of quenching has been shown to be related to the ease of oxidation of the ligand, and calculations according to Rehm–Weller theory of electron transfer quenching show good agreement with the experimental results.

## Experimental

### General

All reagents and solvents were of commercial quality and were dried where necessary using standard procedures. <sup>1</sup>H NMR spectra were obtained on either a Varian VXR400S or a Varian Inova 500 spectrometer, operating at 400 and 500 MHz respectively, and <sup>13</sup>C NMR spectra were obtained on the same machines operating at 100 and 125 MHz. Chemical shifts are quoted in ppm relative to tetramethylsilane, using the high frequency positive convention, and  $J$  values are given in Hz. Mass spectra were recorded on a Micromass LCT spectrometer using electrospray ionization. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected.

### Silicon phthalocyanine bis-(4-*tert*-butyl)benzoate (**3**)

4-*tert*-Butylbenzoic acid (**2**) (0.20 g, 1.12 mmol) and silicon phthalocyanine dichloride (**1**) (0.20 g, 0.32 mmol, purchased from Aldrich) were stirred together in 2-methoxyethyl ether (2 cm<sup>3</sup>) at 160 °C for 3 h. Quenching of the reaction mixture in water (25 cm<sup>3</sup>), followed by filtration of the resulting precipitate gave *silicon phthalocyanine bis-(4-tert-butyl)benzoate* (**3**) as a dark blue-green solid (0.11 g, 39%) after column chromatography over silica gel (eluent DCM). mp >300 °C; (Found:  $[\text{M} + \text{Na}]^+$ , 917.3000; C<sub>54</sub>H<sub>42</sub>N<sub>8</sub>O<sub>4</sub>Si requires  $[\text{M} + \text{Na}]^+$ , 917.2996, error of 0.4 ppm); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 0.73 (18H, s, CH<sub>3</sub>), 5.07 (4H, d, <sup>3</sup>J<sub>HH</sub> 8.8, ArH), 6.25 (4H, d, <sup>3</sup>J<sub>HH</sub> 8.8, ArH), 8.37 (8H, m, PcH), 9.71 (8H, m, PcH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 30.55 (m, CH<sub>3</sub>), 34.18 (s, CMe<sub>3</sub>), 123.89 (s, ArH), 124.31 (s, PcH), 125.48 (s, Ar), 127.53 (s, ArH), 130.06 (s, Ar), 131.49 (s, PcH), 135.81 (s, Pe), 150.47 (s, Pc), 159.16 (s, CO<sub>2</sub>);  $m/z$  (ES<sup>+</sup>) 917, 918, 919 ( $[\text{M} + \text{Na}]^+$ ).

### Silicon phthalocyanine bis-(3-thienyl)acetate (**5**)

Thiophene-3-acetic acid (**4**) (0.39 g, 2.45 mmol) and silicon phthalocyanine dichloride (**1**) (0.30 g, 0.49 mmol) were reacted as above to give *silicon phthalocyanine bis-(3-thienyl)acetate* (**5**) as a dark blue solid (0.14 g, 35%) after column chromatography over silica gel (eluent DCM). mp >300 °C; (Found:  $[\text{M} + \text{Na}]^+$ , 845.1163; C<sub>44</sub>H<sub>26</sub>N<sub>8</sub>O<sub>4</sub>Si<sub>2</sub> requires  $[\text{M} + \text{Na}]^+$ , 845.1185, error of 2.7 ppm); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 0.65 (2H, s, CH<sub>2</sub>), 4.41 (1H, d, <sup>3</sup>J<sub>HH</sub> 5.0, CHCHS), 4.94 (1H, s, CCHS), 6.06 (1H, m, CHCHS), 8.31 (4H, m, PcH), 9.58 (4H, m, PcH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 34.97 (s, CH<sub>2</sub>), 118.94 (s, CCHS), 122.84 (s, CHCHS), 122.99 (s, PcH), 125.04 (s, CHCHS), 130.14 (s, PcH), 131.48 (s, CCH<sub>2</sub>), 134.51 (s, Pc), 148.83 (s, Pc), 163.19 (s, CO<sub>2</sub>);

$m/z$  ( $ES^+$ ) 822, 823, 824, 825 ( $[M]^+$ ), 845, 846, 847, 848 ( $[M + Na]^+$ ), 861, 862, 863 ( $[M + K]^+$ ).

#### Silicon phthalocyanine bis-(2-methoxyphenyl)acetate (7)

(2-Methoxyphenyl)acetic acid (**6**) (0.55 g, 3.31 mmol) and silicon phthalocyanine dichloride (**1**) (0.50 g, 0.82 mmol) were reacted as above to give *silicon phthalocyanine bis-(2-methoxyphenyl)acetate* (**7**) as a dark blue solid (0.17 g, 24%) after column chromatography over silica gel (eluent 3% MeOH in DCM). mp >300 °C; (Found: C, 68.66%; H, 3.86; N, 12.84;  $C_{50}H_{34}N_8O_6Si$  requires C, 68.95; H, 3.93; N, 12.87);  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 0.70 (2H, s,  $CH_2$ ), 2.76 (3H, s,  $CH_3$ ), 4.86 (1H, d m,  $^3J_{HH}$  7.2, ArH), 5.77 (2H, t,  $^3J_{HH}$  8.0, ArH), 6.34 (1H, t m,  $^3J_{HH}$  7.6, ArH), 8.36 (4H, m, PcH), 9.62 (4H, m, PcH);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) 36.05 (s,  $CH_2$ ), 53.77 (s,  $CH_3$ ), 108.57 (s, ArH), 118.76 (s, ArH), 121.91 (s, ArCH<sub>2</sub>), 123.79 (s, PcH), 126.57 (s, ArH), 128.24 (s, ArH), 130.80 (s, PcH), 135.59 (s, Pc), 149.65 (s, Pc), 154.85 (s, ArO), 164.46 (s, CO<sub>2</sub>);  $m/z$  ( $ES^+$ ) 869, 870, 871, 872 ( $[M]^+$ ), 892, 893, 894, 895 ( $[M + Na]^+$ ), 908, 909, 910 ( $[M + K]^+$ ).

#### Silicon phthalocyanine bis-(3-methoxyphenyl)acetate (9)

(3-Methoxyphenyl)acetic acid (**8**) (0.55 g, 3.31 mmol) and silicon phthalocyanine dichloride (**1**) (0.50 g, 0.82 mmol) reacted as above to give *silicon phthalocyanine bis-(3-methoxyphenyl)acetate* (**9**) as a dark blue solid (0.15 g, 21%) after column chromatography over silica gel (eluent 5% MeOH in DCM). mp 288–290 °C; (Found:  $[M + Na]^+$ , 893.2261;  $C_{50}H_{34}N_8O_6Si$  requires  $[M + Na]^+$ , 893.2268, error of 0.8 ppm);  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 0.65 (2H, s,  $CH_2$ ), 3.23 (3H, s,  $CH_3$ ), 4.34 (1H, m, ArH), 4.46 (2H, s, ArH), 6.08 (2H, m, ArH), 8.38 (4H, m, PcH), 9.62 (4H, m, PcH);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) 41.83 (s,  $CH_2$ ), 54.46 (s,  $CH_3$ ), 110.75 (s, ArH), 112.22 (s, ArH), 118.92 (s, ArH), 123.86 (s, PcH), 128.03 (s, ArH), 131.01 (s, PcH), 134.25 (s, ArCH<sub>2</sub>), 135.43 (s, Pc), 149.72 (s, Pc), 158.17 (s, ArO), 164.61 (s, CO<sub>2</sub>);  $m/z$  ( $ES^+$ ) 893, 894, 895, 896 ( $[M + Na]^+$ ).

#### Silicon phthalocyanine bis-(4-methoxyphenyl)acetate (11)

(4-Methoxyphenyl)acetic acid (**10**) (0.55 g, 3.31 mmol) and silicon phthalocyanine dichloride (**1**) (0.50 g, 0.82 mmol) were reacted as above to give *silicon phthalocyanine bis-(4-methoxyphenyl)acetate* (**11**) as a dark blue solid (0.12 g, 17%) after column chromatography over silica gel (eluent 3% MeOH in DCM). mp >300 °C; (Found:  $[M + Na]^+$ , 893.2267;  $C_{50}H_{34}N_8O_6Si$  requires  $[M + Na]^+$ , 893.2268, error of 0.1 ppm);  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 0.60 (2H, s,  $CH_2$ ), 3.62 (3H, s,  $CH_3$ ), 4.72 (2H, d,  $^3J_{HH}$  6.8, ArH), 5.78 (2H, d,  $^3J_{HH}$  6.8, ArH), 8.38 (4H, m, PcH), 9.63 (4H, m, PcH);  $m/z$  ( $ES^+$ ) 870, 871, 872 ( $[M]^+$ ), 893, 894, 895, 896 ( $[M + Na]^+$ ), 909, 910 ( $[M + K]^+$ ).

#### Silicon phthalocyanine bis-(2,5-dimethoxyphenyl)acetate (13)

(2,5-Dimethoxyphenyl)acetic acid (**12**) (0.39 g, 1.99 mmol) and silicon phthalocyanine dichloride (**1**) (0.30 g, 0.49 mmol) were reacted as above to give *silicon phthalocyanine bis-(2,5-dimethoxyphenyl)acetate* (**13**) as a dark blue solid (0.16 g, 35%) after column chromatography over silica gel (eluent 3% MeOH in DCM). mp >300 °C; (Found:  $[M + Na]^+$ , 953.2515;  $C_{52}H_{38}N_8O_8Si$  requires  $[M + Na]^+$ , 953.2480, error of 3.7 ppm);  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 0.69 (2H, s,  $CH_2$ ), 2.71 (3H, s,  $CH_3$ ), 3.26 (3H, s,  $CH_3$ ), 4.46 (1H, d,  $^4J_{HH}$  3.2, CHCCH<sub>2</sub>), 5.63 (1H, d,  $^3J_{HH}$  8.8, CHCOCCH<sub>2</sub>), 5.84 (1H, d d,  $^3J_{HH}$  8.8,  $^4J_{HH}$  3.2, CHCOCCH<sub>2</sub>), 8.37 (4H, m, PcH), 9.62 (4H, m, PcH);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) 35.15 (s,  $CH_2$ ), 53.20 (s,  $CH_3$ ), 54.02 (s,  $CH_3$ ), 109.60 (s, ArH), 112.05 (s, ArH), 113.13 (s, ArH), 122.56 (s, ArCH<sub>2</sub>), 123.76 (s, PcH), 130.88 (s, PcH), 135.55 (s, Pc), 149.02 (s, ArO), 149.66 (s, Pc), 151.63 (s, ArO), 164.28 (s, CO<sub>2</sub>);  $m/z$  ( $ES^+$ ) 931, 932, 933 ( $[M]^+$ ).

#### Silicon phthalocyanine bis-(3,4-dimethoxyphenyl)acetate (15)

(3,4-Dimethoxyphenyl)acetic acid (**14**) (0.39 g, 1.99 mmol) and silicon phthalocyanine dichloride (**1**) (0.30 g, 0.49 mmol) were reacted as above to give *silicon phthalocyanine bis-(3,4-dimethoxyphenyl)acetate* (**15**) as a dark blue solid (0.13 g, 28%) after column chromatography over silica gel (eluent 3% MeOH in DCM). mp 294–297 °C; (Found:  $[M + Na]^+$ , 953.2504;  $C_{52}H_{38}N_8O_8Si$  requires  $[M + Na]^+$ , 953.2480, error of 2.6 ppm);  $^1H$  NMR (500 MHz,  $CDCl_3$ ) 0.61 (2H, s,  $CH_2$ ), 3.16 (3H, s,  $CH_3$ ), 3.69 (3H, s,  $CH_3$ ), 4.32 (1H, d,  $^3J_{HH}$  7.5, CHCHCO), 4.47 (1H, s, CCHC), 5.65 (1H, d,  $^3J_{HH}$  7.5, CHCHCO), 8.39 (4H, m, PcH), 9.63 (4H, m, PcH);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ) 41.63 (s,  $CH_2$ ), 55.20 (s,  $CH_3$ ), 55.67 (s,  $CH_3$ ), 109.46 (s, ArH), 109.72 (s, ArH), 118.87 (s, ArH), 124.05 (s, PcH), 125.59 (s, ArCH<sub>2</sub>), 131.32 (s, PcH), 135.61 (s, Pc), 146.77 (s, ArO), 147.72 (s, ArO), 149.97 (s, Pc), 165.33 (s, CO<sub>2</sub>);  $m/z$  ( $ES^+$ ) 930, 931, 932, 933 ( $[M]^+$ ), 953, 954, 955, 956 ( $[M + Na]^+$ ), 969, 970, 971 ( $[M + K]^+$ ).

#### Silicon phthalocyanine bis-(3,4,5-trimethoxyphenyl)acetate (17)

(3,4,5-Trimethoxyphenyl)acetic acid (**16**) (0.45 g, 1.99 mmol) and silicon phthalocyanine dichloride (**1**) (0.30 g, 0.49 mmol) were reacted as above to give *silicon phthalocyanine bis-(3,4,5-trimethoxyphenyl)acetate* (**17**) as a dark blue solid (0.12 g, 25%) after column chromatography over silica gel (eluent 2% MeOH in DCM). mp >300 °C; (Found:  $[M + Na]^+$ , 1013.2666;  $C_{54}H_{42}N_8O_{10}Si$  requires  $[M + Na]^+$ , 1013.2691, error of 2.5 ppm);  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 0.58 (2H, s,  $CH_2$ ), 3.39 (6H, s,  $CH_3$ ), 3.97 (3H, s,  $CH_3$ ), 4.14 (2H, s, ArH), 8.39 (4H, m, PcH), 9.62 (4H, m, PcH);  $m/z$  ( $ES^+$ ) 991, 992, 993 ( $[M]^+$ ), 1013, 1014, 1015, 1016 ( $[M + Na]^+$ ).

#### Silicon phthalocyanine bis-(3,4-dimethoxy)benzoate (19)

3,4-Dimethoxybenzoic acid (**18**) (0.36 g, 1.98 mmol) and silicon phthalocyanine dichloride (**1**) (0.30 g, 0.49 mmol) were reacted as above to give *silicon phthalocyanine bis-(3,4-dimethoxy)benzoate* (**19**) as a dark blue solid (0.15 g, 34%) after column chromatography over silica gel (eluent 2% MeOH in DCM). mp >300 °C; (Found:  $[M + Na - (MeOH)]^+$ , 893.1865;  $C_{50}H_{34}N_8O_6Si$  requires  $[M + Na - (MeOH)]^+$ , 893.1904, error of 4.4 ppm);  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 2.88 (3H, s,  $CH_3$ ), 3.32 (3H, s,  $CH_3$ ), 4.55 (1H, s, ArH), 4.68 (1H, s, ArH), 5.69 (1H, s, ArH), 8.38 (4H, m, PcH), 9.71 (4H, m, PcH);  $m/z$  ( $ES^+$ ) 871, 872, 873 ( $[M - (MeOH)]^+$ ), 893, 894, 895, 896 ( $[M + Na - (MeOH)]^+$ ), 909, 910, 911, 912 ( $[M + K - (MeOH)]^+$ ).

#### Silicon phthalocyanine bis-3-(3,4-dimethoxyphenyl)propanoate (21)

3-(3,4-Dimethoxyphenyl)propanoic acid (**20**) (0.41 g, 1.95 mmol) and silicon phthalocyanine dichloride (**1**) (0.30 g, 0.49 mmol) were reacted as above to give *silicon phthalocyanine bis-3-(3,4-dimethoxyphenyl)propanoate* (**21**) as a dark blue solid (0.18 g, 38%) after column chromatography over silica gel (eluent 5% MeOH in DCM). mp 268–271 °C; (Found:  $[M + Na]^+$ , 981.2782;  $C_{54}H_{42}N_8O_8Si$  requires  $[M + Na]^+$ , 981.2793, error of 1.1 ppm);  $^1H$  NMR (500 MHz,  $CDCl_3$ ) –0.34 (2H, t,  $^3J_{HH}$  7.5,  $CH_2CO_2$ ), 0.44 (2H, t,  $^3J_{HH}$  7.5,  $CH_2CH_2CO_2$ ), 3.27 (3H, s,  $CH_3$ ), 3.73 (3H, s,  $CH_3$ ), 5.02 (1H, d,  $^3J_{HH}$  8.0, CHCHCO), 5.25 (1H, s, CCHC), 6.09 (1H, d,  $^3J_{HH}$  8.0, CHCHCO), 8.39 (4H, m, PcH), 9.67 (4H, m, PcH);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ) 28.07 (s,  $CH_2CO_2$ ), 34.81 (s,  $CH_2CH_2CO_2$ ), 55.13 (s,  $CH_3$ ), 55.66 (s,  $CH_3$ ), 109.67 (s, ArH), 110.24 (s, ArH), 118.03 (s, ArH), 123.90 (s, PcH), 131.22 (s, PcH), 131.79 (s, ArCH<sub>2</sub>), 135.47 (s, Pc), 146.37 (s, ArO), 147.87 (s, ArO), 149.93 (s, Pc), 166.28 (s, CO<sub>2</sub>);  $m/z$  ( $ES^+$ ) 958, 959, 960, 961 ( $[M]^+$ ), 981, 982, 983, 984 ( $[M + Na]^+$ ), 997, 998, 999 ( $[M + K]^+$ ).

Table 5 Crystal data

	3	5	21
Empirical formula	C <sub>54</sub> H <sub>42</sub> N <sub>8</sub> O <sub>4</sub> Si	C <sub>44</sub> H <sub>26</sub> N <sub>8</sub> O <sub>4</sub> S <sub>2</sub> Si	C <sub>54</sub> H <sub>42</sub> N <sub>8</sub> O <sub>8</sub> Si
Formula weight	895.05	822.94	959.05
Temperature/K	108	110	105
Crystal system	Rhombohedral	Monoclinic	Triclinic
Space group (no.)	R $\bar{3}$ , #148	P2 <sub>1</sub> /c, #14	P $\bar{1}$ , #2
<i>a</i> /Å	36.327(8)	10.078(1)	9.730(1)
<i>b</i> /Å	36.327(8)	22.591(2)	10.118(1)
<i>c</i> /Å	8.841(2)	8.243(1)	13.580(1)
<i>a</i> °	90	90	69.94(1)
<i>β</i> °	90	101.59(1)	88.48(1)
<i>γ</i> °	120	90	61.66(1)
Volume/Å <sup>3</sup>	10104(4)	1838.4(3)	1090.2(2)
<i>Z</i>	9	2	1
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.324	1.487	1.461
<i>μ</i> /mm <sup>-1</sup>	0.11	0.24	0.13
Reflections collected	20515	22354	14155
Unique reflections	5166	4869	5712
<i>R</i> <sub>int</sub>	0.082	0.038	0.029
Refls. with <i>I</i> > 2σ( <i>I</i> )	3259	4025	4894
No. parameters	310	269	339
<i>R</i> [ <i>I</i> > 2σ( <i>I</i> )]	0.047	0.040	0.038
<i>wR</i> ( <i>F</i> <sup>2</sup> ), all data	0.117	0.110	0.104

### Silicon phthalocyanine bis-4-(3,4-dimethoxyphenyl)butanoate (23)

4-(3,4-Dimethoxyphenyl)butyric acid (**22**) (0.41 g, 1.83 mmol) and silicon phthalocyanine dichloride (**1**) (0.30 g, 0.49 mmol) were reacted as above to give silicon phthalocyanine bis-4-(3,4-dimethoxyphenyl)butanoate (**23**) as a dark blue solid (0.12 g, 25%) after column chromatography over silica gel (eluent 5% MeOH in DCM). mp 285–288 °C; (Found: [M + Na]<sup>+</sup>, 1009.3063; C<sub>56</sub>H<sub>46</sub>N<sub>8</sub>O<sub>8</sub>Si requires [M + Na]<sup>+</sup>, 1009.3106, error of 4.2 ppm); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) –0.56 (2H, m, CH<sub>2</sub>CO<sub>2</sub>), 0.68 (2H, m, CH<sub>2</sub>), 0.85 (2H, m, CH<sub>2</sub>Ar), 3.52 (3H, s, CH<sub>3</sub>), 3.70 (3H, s, CH<sub>3</sub>), 5.53 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.1, ArH), 5.68 (1H, s, ArH), 6.28 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.1, ArH), 8.37 (4H, m, PcH), 9.67 (4H, m, PcH); *m/z* (ES<sup>+</sup>) 987, 988, 989 ([M]<sup>+</sup>), 1009, 1010, 1011, 1012 ([M + Na]<sup>+</sup>), 1025, 1026, 1027 ([M + K]<sup>+</sup>).

### X-Ray crystallography

Single crystals were obtained by slow diffusion of hexane into a DCM solution of **3**, **5** or **21**. X-ray diffraction experiments were carried out on a SMART 3-circle diffractometer with a CCD area detector, using graphite-monochromated Mo-Kα radiation ( $\lambda = 0.71073$  Å) and a Cryostream (Oxford Cryosystems) open-flow N<sub>2</sub> gas cryostat. A hemisphere (**3**) or full sphere (**5**, **21**) of reciprocal space was covered by a combination of (respectively) 3 or 5 sets of  $\omega$  scans; each set at different  $\phi$  and/or  $2\theta$  angles. The structures were solved by direct methods and refined by full-matrix least squares against *F*<sup>2</sup> of all data, using SHELXTL software.<sup>35</sup> Crystal data and experimental details are summarized in Table 5, full structural information has been deposited with the Cambridge Crystallographic Data Centre. †

### UV/Vis and fluorescence

Background corrected UV-Vis absorption spectra were recorded on a Unicam UV2 UV-Vis spectrometer controlled by a PC using Vision 3.50 software. Fluorescence spectra were recorded on either a Spex Fluorolog 2 spectrofluorimeter, a Spex Fluoromax 2 spectrofluorimeter or a Perkin Elmer LS-50B luminescence spectrometer and were corrected for the spectral response of the machine. Lifetimes were recorded using

the technique of time correlated single photon counting,<sup>36</sup> details of which we have published previously.<sup>37</sup> Quantum yields were determined by the comparative method of Williams *et al.*,<sup>38</sup> measurements being taken using several dilutions of each sample to negate concentration effects. Cresyl violet ( $\phi_F = 0.54$ ) and disulfonated aluminium pc ( $\phi_F = 0.40$ ) were used as standards.

### Cyclic voltammetry

Cyclic voltammetry experiments were recorded using an EG&G Versastat II instrument in MeCN containing 0.1 M [NBu<sub>4</sub>]BF<sub>4</sub>. Solutions were purged with argon and measured with a platinum working electrode with platinum wire reference and counter electrodes at room temperature. Oxidation potentials obtained were referenced using the ferrocene–ferrocenium redox couple (0.40 V vs. SCE)<sup>39</sup> and are quoted vs. NHE, *E*(SCE) = 0.24 V vs. NHE.

### CAChe

The computer program CAChe (Oxford Molecular, Ltd.) was used to perform structural optimisation of the structures of the phthalocyanine compounds. The MM3 algorithm was used for the MOPAC structural optimisations, using the standard procedure for energy minimisation.

### Acknowledgements

The authors thank M. Jones and L. M. Turner for assistance with the mass spectroscopy and accurate mass measurements of the compounds, A. Kenwright, I. H. McKeag and C. F. Hefferman for running the NMR spectra and P. J. Low, O. Koentjoro and M. Paterson for assistance with CV measurements. We also thank EPSRC for funding CF, SF and X-ray instrumentation, and J. A. K. Howard for helpful crystallographic advice.

### References

- Reviews: (a) *Phthalocyanine Compounds*, ed. F. H. Moser and A. L. Thomas, Reinhold, New York, 1963; (b) *Phthalocyanines, Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, vols. 1–4, VCH, New York, 1989–1996; (c) N. B. McKeown, *Chem. Ind.*, 1999, 92.
- (a) L. J. Boucher, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum Press, New York, 1979,

† CCDC reference numbers 171718 (**3**), 171719 (**5**) and 171720 (**21**). See <http://www.rsc.org/suppdata/p2/b1/b108778a/> for crystallographic files in .cif or other electronic format.

- 461–516; (b) N. B. McKeown, *Phthalocyanine Materials, Synthesis, Structure and Function*, Cambridge University Press, Cambridge.
- 3 (a) I. Rosenthal, *J. Photochem. Photobiol.*, 1991, **53**, 859; (b) P. K. Panday and C. K. Herman, *Chem. Ind.*, 1998, 739.
- 4 (a) R. J. Mortimer, *Electrochim. Acta*, 1999, **44**, 2971; (b) R. J. Mortimer, *Chem. Soc. Rev.*, 1997, **26**, 147; (c) C. H. Chen, J. Shi and C. W. Tang, *Macromol. Symp.*, 1997, **125**, 1.
- 5 H. S. Nalwa and J. S. Shirk, in *Phthalocyanines, Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, vol. 4, VCH, New York, 1996, 83–181; and references therein.
- 6 (a) R. F. Parton, I. F. J. Van Keulecom, M. J. A. Bezoukhanova and P. A. Jacobs, *Nature*, 1994, **370**, 541; (b) A. B. P. Lever, M. R. Hempstead, C. C. Leznoff, W. Liu, M. Melnik, W. A. Nevin and P. Seymour, *Pure Appl. Chem.*, 1986, **58**, 1467.
- 7 (a) J. H. Zagal, *J. Electroanal. Chem.*, 1980, **109**, 389; (b) T. Kilcuchi, H. Sasaki and S. Toshima, *Chem. Lett.*, 1980, 5.
- 8 (a) A. N. Cammidge, M. J. Cook, K. J. Harrison and N. B. McKeown, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3053; (b) J. F. Van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Notte, W. Drenth, J. Aerts, R. Visser and S. J. Picken, *Liq. Cryst.*, 1989, **6**, 577; (c) K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio and J. Simon, *New J. Chem.*, 1988, **12**, 751.
- 9 (a) M. K. Nazeeruddin, R. Humphry-Baker, M. Gratzel and B. A. Murrer, *Chem. Commun.*, 1998, 719; (b) J. B. Whitlock, P. Panayotatos, G. D. Sharma, M. D. Cox, R. R. Sauer and G. R. Bird, *Opt. Eng.*, 1993, **32**, 1921; (c) D. Wohrle and D. Meissner, *Adv. Mater.*, 1991, **3**, 129.
- 10 R. C. Ahuja and K. Hauffe, *Ber., Bunsenges. Phys. Chem.*, 1980, **84**, 68 and references therein.
- 11 D. Lelievre, O. Damette and J. Simon, *J. Chem. Soc., Chem. Commun.*, 1993, 939.
- 12 (a) N. Kobayashi, Y. Higashi and T. Osa, *J. Chem. Soc., Chem. Commun.*, 1994, 1785; (b) B. Mohr, G. Wegner and K. Ohta, *J. Chem. Soc., Chem. Commun.*, 1995, 995; (c) M. J. Cook and A. Jafari-Fini, *J. Mater. Chem.*, 1997, **7**, 5; (d) D. M. Knawby and T. M. Swager, *Chem. Mater.*, 1997, **9**, 535.
- 13 (a) T. G. Linßen, K. Durr, M. Hanack and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, 1995, 103; (b) K. Durr, S. Fielder, T. G. Linßen, A. Hirsch and M. Hanack, *Chem. Ber. Rec.*, 1997, **130**, 1375.
- 14 M. J. Cook, G. Cook and A. Jafari-Fini, *J. Chem. Soc., Chem. Commun.*, 1995, 1715.
- 15 (a) C. F. Van Nostrum, S. J. Picken, A. J. Schouten and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1995, **117**, 9957; (b) C. F. Van Nostrum and R. J. M. Nolte, *Chem. Commun.*, 1996, 2385.
- 16 M. Kimura, T. Hamakawa, T. Muto, K. Hanabusa, H. Shirai and N. Kobayashi, *Tetrahedron Lett.*, 1998, **39**, 8471.
- 17 (a) M. A. Blower, M. R. Bryce and W. Devonport, *Adv. Mater.*, 1996, **8**, 63; (b) C. Wang, M. R. Bryce, A. S. Batsanov, C. F. Stanley, A. Beeby and J. A. K. Howard, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1671; (c) M. J. Cook, G. Cook and A. Jafari-Fini, *Chem. Commun.*, 1996, 1925.
- 18 (a) M. Brewis, G. J. Clarkson, A. M. Holder and N. B. McKeown, *Chem. Commun.*, 1998, 1979; (b) A. C. H. Ng, X.-Y. Li and D. K. P. Ng, *Macromolecules*, 1999, **32**, 5292.
- 19 P. Mallard, J.-L. Guerquin-Kern, M. Momenteau and S. Gaspard, *J. Am. Chem. Soc.*, 1989, **111**, 9125.
- 20 X.-Y. Li and D. K. P. Ng, *Tetrahedron Lett.*, 2001, **42**, 305.
- 21 (a) R. Dong, Y. Qiu, S. Tian, S. Wang and X. Song, *Sci. China (Ser. B)*, 1998, **41**, 45; (b) U. Drechsler, M. Pfaff and M. Hanack, *Eur. J. Org. Chem.*, 1999, 3441.
- 22 N. B. McKeown, *J. Mater. Chem.*, 2000, **10**, 1979.
- 23 (a) S. Dhama and D. Phillips, *J. Photochem. Photobiol. A: Chem.*, 1996, **100**, 77; (b) K. Lang, P. Kubat, J. Mosinger and D. Wagnerova, *J. Photochem. Photobiol. A: Chem.*, 1998, **119**, 47.
- 24 R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, 1962, 236.
- 25 M. Brewis, G. J. Jackson, V. Goddard, M. Helliwell, A. M. Holder and N. B. McKeown, *Angew. Chem., Int. Ed.*, 1998, **37**, 1092.
- 26 T. Muto, T. Temma, M. Kimura, K. Hanabusa and H. Shirai, *Chem. Commun.*, 2000, 1649.
- 27 (a) W. Kemp, *NMR in Chemistry*, Macmillan, Basingstoke, 1986; (b) H. Gunther, *NMR Spectroscopy*, 2<sup>nd</sup> Edn., J. Wiley and Sons, Chichester, 1995.
- 28 (a) M. Brewis, G. J. Clarkson, V. Goddard, M. Helliwell, A. M. Holder and N. B. McKeown, *Angew. Chem., Int. Ed.*, 1998, **37**, 1092; (b) J. Silver, J. L. Sosa-Sanchez and C. S. Frampton, *Inorg. Chem.*, 1998, **37**, 411; (c) R. Decreau, M. Julliard and M. Giorgi, *Acta Crystallogr., Sect. C*, 1999, **55**, 1717.
- 29 S. M. Aldoshin, O. A. D'yachenko, L. O. Atovmyan, A. N. Chekhlov and M. I. Aldoshin, *Koord. Khim.*, 1980, **6**, 936.
- 30 K. A. Bello and I. A. Bello, *Dyes Pigm.*, 1997, **35**, 261.
- 31 J. R. Darwent, I. McCubbin and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 903.
- 32 T. Ohno, S. Kato and N. N. Lichtin, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2753.
- 33 M. E. Daraio, A. Volker, P. F. Aramendia and E. San Roman, *Langmuir*, 1996, **12**, 2932.
- 34 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 1982.
- 35 SHELXTL, Version 5.1, Bruker AXS Inc., Madison, WI, USA, 1997.
- 36 D. V. O'Connor and D. Phillips, *Time Corrected Single Photon Counting*, Academic Press, London, 1984.
- 37 A. Beeby, S. FitzGerald and C. F. Stanley, *Photochem. Photobiol.*, 2001, **74**, 566.
- 38 A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067.
- 39 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.