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Synthesis of new axially-disubstituted silicon-phthalocyanine derivatives: optical and structural characterisation

Carl A. Barker, Karen S. Findlay, Sylvia Bettington, Andrei S. Batsanov, Igor F. Perepichka, Martin R. Bryce* and Andrew Beeby*

Department of Chemistry, University of Durham, Durham DH1 3LE, UK

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Abstract—This paper describes the synthesis of a range of new axially-disubstituted silicon-phthalocyanines with several ester and ether derivatives as axial ligands, including phenyl, terphenyl, thienyl and pyrenyl systems. Their absorption and emission spectra are reported and fluorescence lifetimes and quantum yields are correlated with the ligand structures. The X-ray crystal structure of a new polymorph of silicon-phthalocyanine bis(3-thienyl)acetate **7** is described.

1. Introduction

Phthalocyanines (Pcs) and related macrocycles are of great interest due to the array of interesting optoelectronic and coordination properties, which they display.[1] They serve as active components in such diverse fields as media for optical data storage,[2] electrochromic[3] and optical limiting devices,[4] multistage-redox-dependent fluorophores,[5] photosensitisers,[6] and medicinal therapeutic agents.[7] Many of the properties of Pcs are highly dependent on the extent of intermolecular π–π stacking interactions between the planar faces of the macrocycles. For example, dimerisation or aggregation (i.e., strong interactions) between neighbouring Pc molecules generally leads to fluorescence quenching and a broadened, blue-shifted principle Q-band due to exciton coupling[8] and can normally be observed even in very dilute solutions. One topic of current interest is the study of Pc derivatives which are not able to aggregate due to special structural features, thereby giving rise to sharply defined UV–vis absorption and emission peaks and higher photoluminescence quantum yields at high concentrations. Examples are provided by axially-substituted metallo-Pcs[9] and derivatives with bulky peripheral substituents, e.g., with rigid spirocyclic fused rings.[10]

Axially-substituted silicon-Pcs have higher quantum yields and longer fluorescence lifetimes than zinc- and aluminium-Pcs, and are therefore more suited to fluorescence studies.[11] We have previously described the synthesis of symmetrical silicon-Pc bis-esters, e.g., compounds **4** and **7**,[12] and analogues containing electroactive tetrathiafulvalene groups.[13] We have now extended this methodology to produce a series of new Si-Pc derivatives, comprising symmetrically- and unsymmetrically-substituted esters and a related bis-ether derivative, **1–11**. The photophysical properties of compounds **1–11** are discussed, along with the X-ray crystal structure of a new polymorph of silicon-phthalocyanine bis(3-thienyl)acetate **7** obtained during the course of this work.

2. Results and discussion

2.1. Synthesis

The synthesis of the target compounds involved the nucleophilic displacement of one or two chloride substituents from either PhSi(Pc)Cl or Si(Pc)Cl_2, respectively, by reaction with the acid or alkoxide derivative of the ligand in 2-methoxyethyl ether or dioxane at high temperature. The structures of compounds **1–11** thereby obtained are shown in Chart 1. The substituent ligands were chosen to probe the effects on the optical properties of the system by varying the aryl substituents and their mode of linkage to the central Si atom. In compounds **1–3**, a phenyl substituent is attached directly to the silicon; compounds **3** and **9** contained phenoxide substituents; all other aryl groups are attached through ester linkages. The aryl groups used in this study are: phenyl (**1–3**, **9**), thienyl (**2**, **5–7**), terphenyl (**8**) and pyrenyl (**10** and **11**). Flexibility was introduced into the ligand structure in compounds **2**, **7**, **10** and **11** by incorporating additional alkyl

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Keywords: Phthalocyanine; Axial ligands; Fluorescence; Crystal structure; Pyrene.

* Corresponding authors. E-mail addresses: m.r.bryce@durham.ac.uk; andrew.beeby@durham.ac.uk

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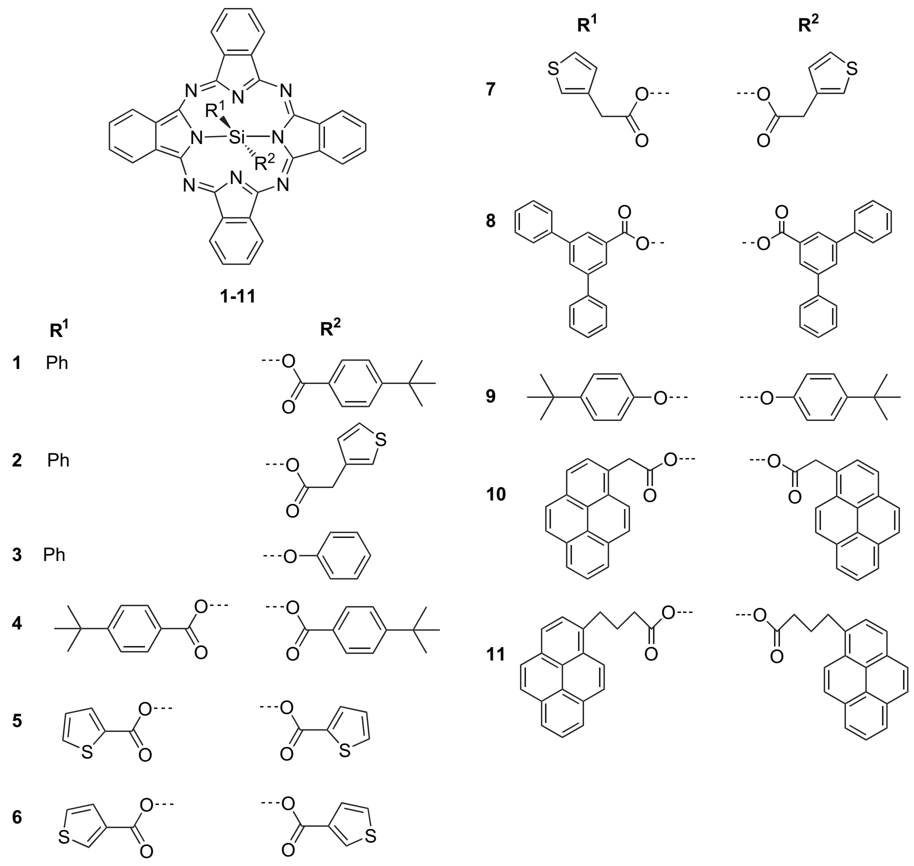

Chart 1. Structures of the axial Pc derivatives studied in this work.

spacers. Compounds **4** and **7** have been reported by us previously[12] and serve as reference materials in the present work.

All the new Pc derivatives were characterised by ^{1}H NMR, solution-state UV–vis absorption and emission spectra, and electrospray ionisation or MALDI-ToF mass spectrometry, with additional ^{13}C NMR spectra and elemental analysis for some compounds; all these data are consistent with the predicted structures. The limited solubility meant that some carbon atoms (especially of the Pc unit) were not observed in the ^{13}C NMR spectra of some of the derivatives even after long acquisition times.

The axially-substituted Pcs have characteristic ^{1}H NMR spectra: the close proximity of the ligand to the large macrocyclic ring current induces a large upfield shift (i.e., to low frequency) in the ligand proton resonances. Thus the five ligand hydrogen atoms of PhSi(Pc)Cl give a doublet at δ 1.56 (2H) and triplets at δ 5.13 (2H) and 5.53 (1H) ppm from the *o*-, *m*- and *p*-Ph protons, respectively. For compound **1** the corresponding resonances are seen at δ 1.82, 5.16 and 5.60 ppm, with two additional doublets from the 4-*tert*-butylbenzoate ligand at δ 4.96 and 6.21 ppm. A comparison of the bis(3-thienyl) derivatives **6** and **7** shows that the additional methylene spacer in the latter has a relatively small effect on the chemical shift of the thienyl ring protons (**6**: δ 4.98, 5.14, 6.12; **7**[12]: 4.41, 4.94, 6.06 ppm).

Within the series (Chart 1), compound **10** gave clear and well-resolved ^{1}H and ^{13}C NMR spectra (Fig. 1). In particular, strong orbital interactions of the pyrene fragments with the Si-Pc core result in pronounced upfield shifts of some of the pyrene protons, which range from δ 8.31 to 5.38 ppm (one proton is overlapped with a Pc signal). For the bis(pyrene) analogue **11** with a longer spacer, the pyrene–Pc orbital overlap is reduced and the furthest upfield pyrene protons are at δ 6.57 ppm.

2.2. X-ray crystal structure of 7

Recrystallisation of **7** by slow diffusion of hexane into a DCM solution of **7** unexpectedly yielded a different polymorph (β-**7**) from the α-**7** polymorph we had obtained previously[12] from the same solvent. Both structures are monoclinic. In α-**7** the Si atom lies at a crystallographic inversion centre in the space group $P2_1/c$, whereas in β-**7** the molecule occupies a general position in the space group $C2/c$ (Fig. 2). The coordination polyhedron of the Si atom is an octahedron compressed along an O···O axis. The mean Si–N distance of 1.904(5) Å is the same as in α-**7** [1.909(3) Å] and other $SiPc(O_2CR)_2$ compounds[12,14–16] (1.900–1.914 Å) but shorter than in Si-Pc without axial ligands (1.946 and 1.965 Å).[17] The SiN_4 coordination is perfectly planar, but the Si-Pc system as a whole is puckered: the average deviation of the 41 non-H atoms from their mean plane is 0.11 Å and the maximum deviation is 0.28 Å (cf. 0.06 and 0.14 Å, respectively, in α-**7**), interplanar angles between the four 'isoindole' moieties vary from 5 to 12° (cf. 0–6° in α-**7**). The carboxy moieties O(1)O(2)C(33)C(34) and O(3)O(4)C(39)C(40) are inclined to the SiN_4 plane by 73 and 83° (cf. 75° in α-**7**), which is rather usual for $SiPc(O_2CR)_2$

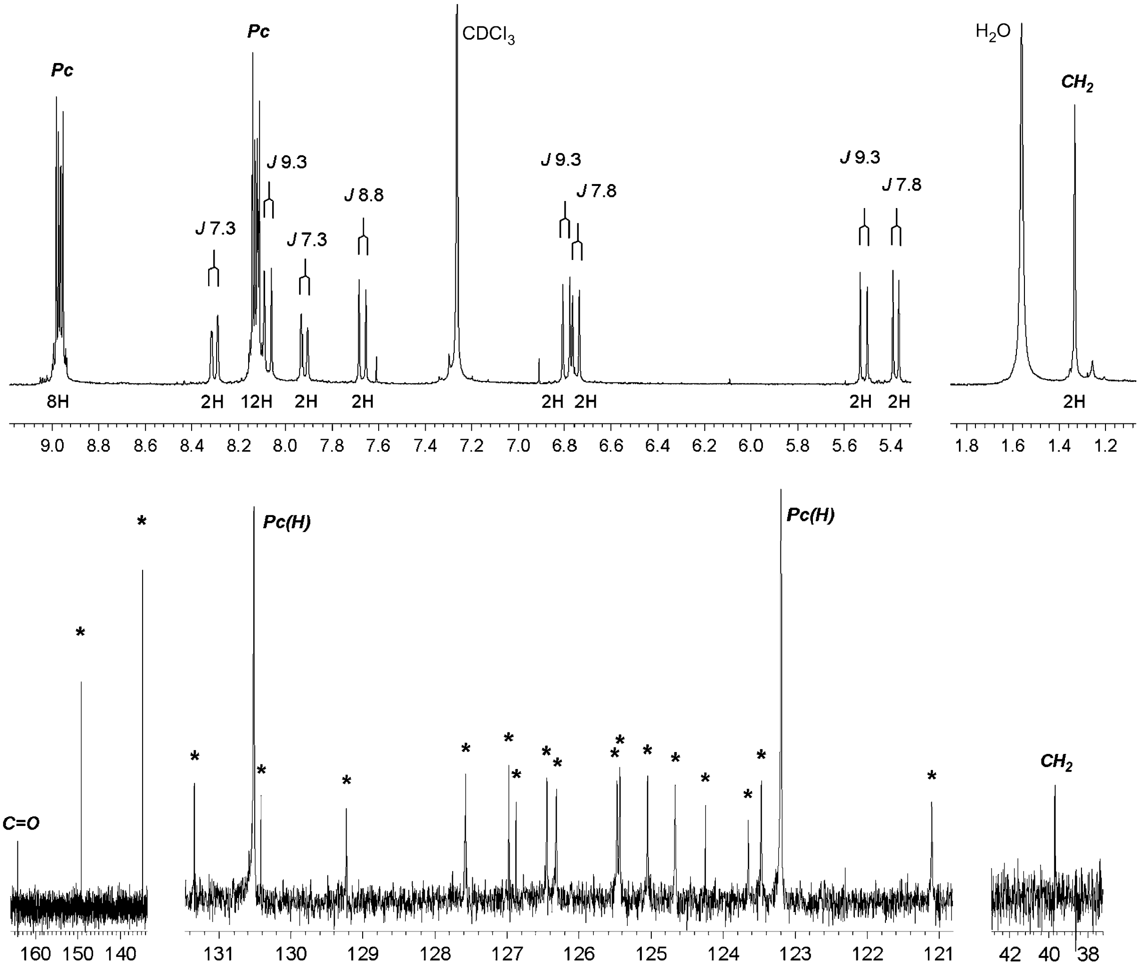

Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **10** in CDCl$_3$.

molecules. However, in other respects the molecular conformations in α-**7** and β-**7** are quite different. In α-**7**, and all other SiPc(O$_2$CR)$_2$ structures, the carboxy groups have a trans orientation with respect to the O–Si–O axis, whether or not the Si atom occupies an inversion centre. In β-**7** the carboxy groups are in a *gauche* orientation, with the O(2)···O(1)···O(3)···O(4) torsion angle of 92°. In α-**7** the thienyl rings are stacked to the phthalocyanine moiety (interplanar angle 11°).

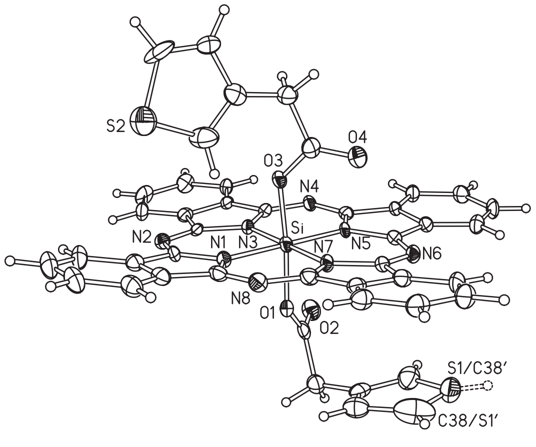

Figure 2. Molecule of **7** in the β polymorph. Selected bond distances (Å): Si–N(1) 1.911(3), Si–N(3) 1.899(3), Si–N(5) 1.900(3), Si–N(7) 1.907(3), Si–O(1) 1.756(3), Si–O(3) 1.778(3).

Such a conformation has been observed previously in all SiPc(O$_2$CR)$_2$ molecules, which had the rotational freedom to adopt it. In β-**7**, one thienyl ring is near-parallel and the other near-perpendicular to the phthalocyanine moiety; the dihedral angles to the SiN$_4$ plane being 8 and 82°, respectively. The Si–O bond lengths in β-**7** differ by 0.02 Å, whereas in its analogues these distances are equal within experimental error, if not symmetrically equal (in the range 1.742–1.758 Å). The 'parallel' thienyl ring in β-**7** (as in α-**7**) is disordered by a 180° rotation around the C(34)–C(36) bond, with S and C atoms statistically mixed in a 3:2 ratio.

2.3. Absorption and fluorescence spectroscopy

The photophysical data for compounds **1**–**11** in dichloromethane (DCM) are collated in Table 1.

All of the Si-Pcs show very sharp electronic absorption transitions in the concentration range 10^{-4}–10^{-7} M (Table 1 and Figs. 3 and 4 for compound **3** and **11** in DCM), which are characteristic of monomeric Si-Pc derivatives.[18] The retention of monomeric behaviour even at 10^{-4} M demonstrates that the axial ligands are very effective in sterically isolating

Table 1. Photophysical data for Si-Pc compounds **1–11**

Compound	λ_{max}^{abs}/nm	λ_{max}^{PL}/nm	Φ_f[a]	τ_{f1}/ns[b]	τ_{f2}/ns[b]
1	685	691	0.55	7.1 (99%)	1.1 (1%)
2	688	696	0.52	6.9 (99%)	1.0 (1%)
3	685	692	0.31	5.8	—
4[12]	685	691	0.62	6.7	—
5	686	689	0.48	6.2 (88%)	2.1 (12%)
6	684	689	0.58	6.3 (86%)	2.4 (14%)
7[12]	685	691	0.39	6.7	—
8	685	691	0.69	6.4 (96.4%)	1.7 (4.6%)
9	680	683	0.06	0.5 (94.7%)	5.4 (5.3%)
10	691	696	0.84	6.9 (99.6%)	0.1 (0.4%)
11	684	691	0.81	6.4 (99.6%)	1.9 (0.4%)

[a] ±10%, λ_{ex}=615 nm, λ_{em}=630–850 nm, 293 K, in DCM.

[b] ±0.1 ns, λ_{ex}=635 nm, λ_{em}=690 nm, 293 K, in DCM.

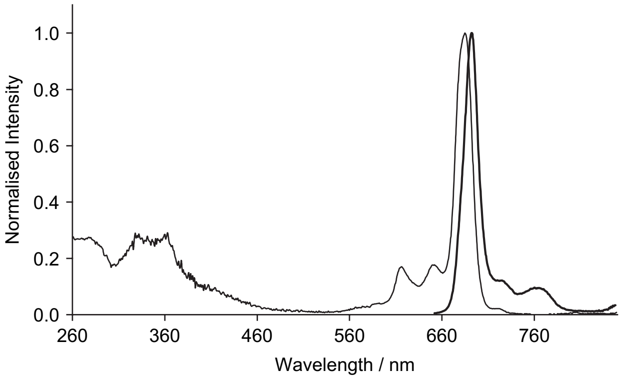

Figure 3. Normalised absorption (thin line) and emission spectra (thick line) of compound **3** in DCM (λ_{ex}=615 nm, same conditions as stated in Table 1).

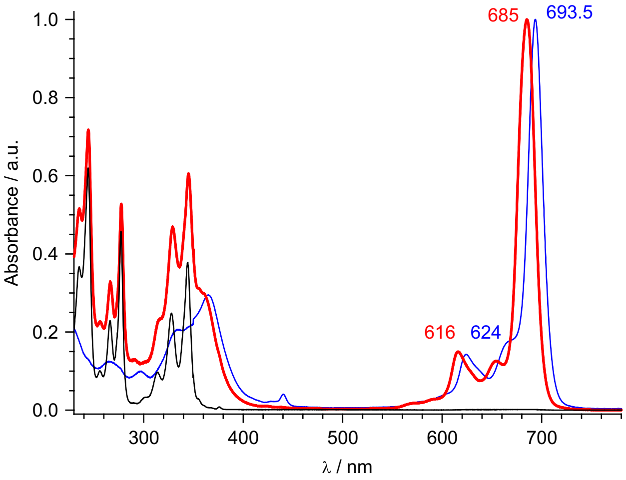

Figure 4. Normalised absorption spectra of compound **11** (thick red line), Si(Pc)Cl_2 (thin blue line) and 1-pyrenebutyric acid (thin black line) in DCM.

the chromophoric Pc rings, by preventing intermolecular interactions between the macrocycles. All the derivatives, **1–11**, show small hypsochromic shifts of their long-wavelength maxima compared to Si(Pc)Cl_2 (by 2–14 nm, Table 1, and Fig. 3). As an example, Figure 4 compares the electron absorption spectra of compound **11** with Si(Pc)Cl_2 and 1-pyrenebutyric acid, demonstrating that the spectrum of **11** combines the spectral features of both the silicon-phthalocyanine and the ligand. The molar extinction coefficients determined for compounds **4**, **8** and **10** in DCM are of the order of ~2×10^5 mol dm^{-3} cm^{-1} at λ_{max} and are consistent with those values found for monomeric phthalocyanines.

Analysis of the emission data in Table 1 shows that the electronic energy levels are relatively unaltered by changing the axial substituents and all of the compounds have a very small Stokes shift of less than 10 nm. In general, the fluorescence quantum yield (Φ_f) and fluorescence lifetime (τ_{f1}) values are high, with the exception of compounds **3**, **5**, **7** and **9**, and are typical of silicon-phthalocyanines.[1] The presence of the lighter Si atom in the macrocycle leads to lower rates of inter-system crossing (ISC) than those observed in other metallo-Pcs, e.g., zinc derivatives.[19] The high Φ_f (>0.5) and long lifetimes (>6 ns) are indicative of efficient fluorescent emission and a fairly small non-radiative decay constant. Compounds **8**, **10** and **11** have the most bulky substituents and possess the highest Φ_f values due to their ability to prevent intermolecular interactions and show no evidence of ligand-macrocycle quenching.

The axial ligands in compounds **5** and **7** contain thiophene and also possess significantly lower Φ_f values. The electron-rich thiophene group may quench the excited state by an electron transfer mechanism resulting in a lower value for Φ_f.[20–24] As shown in Figure 2, if a thiophene ring is allowed to lie close (i.e., parallel) to the Pc macrocycle then electron transfer is more facile. Unusually the lifetimes of **5** and **7** are not reduced by this quenching. The calculated rate constants of fluorescence k_f ($=\Phi_f/\tau_f$) are 7.7×10^7 and 5.8×10^7 s^{-1} for compounds **5** and **7**, respectively, in comparison to that of 7.7×10^7 s^{-1} for compound **1**.

Compounds **3** and **9** also have low Φ_f and τ_f values. The axial phenoxy substituents lead to significant quenching of the phthalocyanine fluorescence, again possibly via an electron transfer process.

3. Conclusions

We have synthesised a range of new silicon-Pc derivatives possessing axial substituents, which effectively prevent aggregation of the Pc chromophores as shown by the very sharp transition in their visible absorption and emission spectra. Altering the axial substituents does not significantly change the λ_{max} values. The luminescence properties are characterised by long lifetimes and high quantum yields, except for compound **9** where the two axial phenoxy substituents lead to significant quenching of the Pc fluorescence, possibly via an electron transfer process. Future work will address new functionalisation modes at the silicon centre and at the periphery of the Pc platform to enable further tuning of the optoelectronic and structural properties of these interesting materials.

4. Experimental

4.1. General

General details of equipment and procedures are the same as those we have reported previously.[12] All synthetic reagents were used as supplied. Solvents were dried and distilled using standard procedures.

4.2. Synthesis

Compounds **4** and **7** were prepared as described previously.[12] Crystals of **7** were obtained by a slow diffusion of hexane into a DCM solution containing **7**.

4.2.1. Phenyl silicon-phthalocyanine chloride [PhSi(Pc)-Cl].[25] 1,3-Diiminoisoindoline (10.0 g, 68.9 mmol) and phenyltrichlorosilane (17.5 mL, 109 mmol) were stirred in a mixture of tetrahydronaphthalene (175 mL) and tributylamine (75 mL) at 215 °C for 20 h. The resultant mixture was allowed to cool and then methanol (100 mL) was added. Filtration of the precipitate followed by copious washing with methanol and diethyl ether gave phenyl silicon-phthalocyanine chloride as a purple solid (6.1 g, 54%) after recrystallisation from toluene; mp>400 °C (Found: C, 69.90%; H, 3.25%; N, 17.16%. $C_{38}H_{21}N_8ClSi$ requires: C, 69.88%; H, 3.24%; N, 17.16%); ^1H NMR (300 MHz, DMSO-d_6): δ 1.56 (2H, d, ^3J=7.8 Hz, *o*-Ph), 5.13 (2H, dd, ^3J=7.5, 7.5 Hz, *m*-Ph), 5.53 (1H, t, ^3J=7.5 Hz, *p*-Ph), 8.53 (8H, m, PcH), 9.68 (8H, m, PcH); IR (Nujol): ν_{max} 2926, 2856, 1464, 1380, 1336, 1286, 1164, 1124, 1080, 908, 727 cm^{-1}; MS (ES$^+$): *m/z* 652, 653, 654 $[M]^+$, 617, 618, 619 $[M-Cl]^+$.

4.2.2. Phenyl silicon-phthalocyanine 4-*tert*-butylbenzoate (1). A mixture of 4-*tert*-butylbenzoic acid (0.055 g, 0.31 mmol) and PhSi(Pc)Cl (0.20 g, 0.31 mmol) was stirred in 2-methoxyethyl ether (8 mL) at 160 °C for 3 h. Quenching of the reaction mixture in water (25 mL), followed by filtration of the resulting precipitate gave a green solid. Unreacted PhSi(Pc)Cl was removed by recrystallisation from toluene, and the filtrate was added to a 5% NaOH solution (150 cm^3). After separation of the layers and washing of the organic layer with water, evaporation of the organic layer to dryness gave **1** as a green solid (0.19 g, 78%); mp>400 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.71 (9H, s, CH_3), 1.82 (2H, d, ^3J=6.9 Hz, *o*-PhH), 4.96 (2H, d, ^3J=8.7 Hz, ArH), 5.16 (2H, dd, ^3J=7.2, 7.2 Hz, *m*-PhH), 5.60 (1H, t, ^3J=7.0 Hz, *p*-PhH), 6.21 (2H, d, ^3J=8.7 Hz, ArH), 8.35 (8H, m, PcH), 9.66 (8H, m, PcH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.06 (CH_3), 41.30 (*C*Me$_3$), 124.36, 131.51, 133.33, 136.35, 150.32, 172.63 (CO_2) [some Pc and Ph peaks were not seen in ^{13}C NMR spectrum]; IR (DCM): ν_{max} 3054, 2988, 2367, 2340, 1420, 1270, 900, 742, 711 cm^{-1}; MS (ES$^+$): *m/z* 817, 818, 819 $[M+Na]^+$; HRMS found: 794.2573, calcd for $C_{49}H_{34}N_8O_2Si$: 794.2574.

4.2.3. Phenyl silicon-phthalocyanine 3-thienylacetate (2). A mixture of thiophene-3-acetic acid (0.044 g, 0.31 mmol) and PhSi(Pc)Cl (0.20 g, 0.31 mmol) was stirred in 2-methoxyethyl ether (8 mL) at 160 °C for 3 h. Workup as described for **1**, gave **2** as a blue solid (0.16 g, 69%); mp>400 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.67 (2H, s, CH_2), 1.73 (2H, d, ^3J=8.1 Hz, *o*-Ph), 4.43 (1H, d, ^3J=3.6 Hz, thiophene-5H), 4.96 (1H, s, thiophene-2H), 5.10 (2H, dd, ^3J=8.3, 7.0 Hz, *m*-Ph), 5.56 (1H, t, ^3J=7.2 Hz, *p*-Ph), 6.11 (1H, d, ^3J=3.7 Hz, thiophene-4H), 8.35 (8H, m, PcH), 9.63 (8H, m, PcH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.34 (CH_2), 112.59, 120.31, 123.60, 124.30, 126.41, 128.78, 131.50, 132.86, 135.88, 136.34, 150.20, 164.54 (CO_2) [one peak was not seen in ^{13}C NMR spectrum]; MS (MALDI-ToF): *m/z* 781, 782, 783 $[M+Na]^+$.

4.2.4. Phenyl silicon-phthalocyanine phenoxide (3). Sodium phenoxide (0.036 g, 0.31 mmol) and PhSi(Pc)Cl (0.20 g, 0.31 mmol) were stirred in 1,4-dioxane (25 mL) at 102 °C for 19 h. Quenching of the reaction mixture in water (25 mL), followed by filtration of the resulting precipitate gave **3** as a dark blue solid (0.15 g, 71%) after recrystallisation from 1,2-dichlorobenzene; mp>400 °C. ^1H NMR (300 MHz, DMSO-d_6): δ 1.55 (2H, d, ^3J=8.1 Hz, *o*-PhH), 5.13 (2H, dd, ^3J=7.8, 6.9 Hz, *m*-PhH), 5.52 (1H, t, ^3J=6.8 Hz, *p*-PhH), 6.78 (2H, d, ^3J=7.8 Hz, ArH), 7.19 (1H, t, ^3J=7.9 Hz, ArH), 8.53 (8H, m, PcH), 9.68 (8H, m, PcH) (2H, ArH, obscured by DMSO peaks); IR (DCM): ν_{max} 3058, 2992, 2367, 2310, 1389, 1270, 900, 746, 711 cm^{-1}; MS (MALDI-ToF): *m/z* 710, 711, 712 $[M]^+$, 633, 634, 635 $[M-Ph]^+$). HRMS found: 710.1997, calcd for $C_{44}H_{26}N_8OSi$: 710.1999.

4.2.5. Silicon-phthalocyanine bis-thiophene-2-carboxylate (5). 2-Thiophene-carboxylic acid (0.21 g, 1.64 mmol) and $Si(Pc)Cl_2$ (0.20 g, 0.33 mmol) were stirred together in 2-methoxyethyl ether (20 mL) at 160 °C for 15 h. Workup as described for **1** gave **5** as a blue solid (0.068 g, 26%); mp>400 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 5.26 (2H, d, ^3J=3.0 Hz, thiophene-3H), 5.94 (2H, dd, ^3J=4.4, 4.4 Hz, thiophene-4H), 6.37 (2H, d, ^3J=4.2, thiophene-5H), 8.39 (8H, m, PcH), 9.71 (8H, m, PcH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.45, 130.45, 131.73, 135.85, 150.57 [no Pc peaks were seen in ^{13}C NMR spectrum]; IR (DCM): ν_{max} 3054, 1592, 1527, 1389, 1336, 1270, 1068, 817, 746, 707 cm^{-1}; MS (MALDI-ToF): *m/z* 794, 795, 796 [M^+], 667, 668, 669 $[M-ThCO_2]^+$; HRMS found: 794.0976, calcd for $C_{42}H_{22}N_8O_4S_2Si$: 794.0975.

4.2.6. Silicon-phthalocyanine bis-thiophene-3-carboxylate (6). Following the procedure for **5**, 3-thiophene-carboxylic acid (0.21 g, 0.33 mmol) and $Si(Pc)Cl_2$ (0.2 g, 0.33 mmol) gave **6** (0.045 g, 17%); mp>400 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 4.98 (2H, m, thiophene-5H), 5.14 (2H, s, thiophene-2H), 6.12 (2H, m, thiophene-4H), 8.40 (8H, m, PcH), 9.71 (8H, m, PcH) [thienyl-2,4 proton peaks could not be cleanly resolved and are listed as multiplets]; MS (ES$^+$): *m/z* 794, 795, 796 ($[M]^+$), 667, 668, 669 $[M-ThCO_2]^+$; HRMS found: 794.0975, calcd for $C_{42}H_{22}N_8O_4S_2Si$: 794.0975.

4.2.7. 3,5-Diphenylbenzoic acid. Benzeneboronic acid (1.00 g, 8.20 mmol), 3,5-dibromobenzoic acid (1.10 g, 3.92 mmol), $Pd(PPh_3)_2Cl_2$ (0.58 g, 0.83 mmol) and degassed THF (100 mL) were stirred at room temperature for ca. 30 min. Degassed aqueous Na_2CO_3 solution (15 mL) was added and the mixture was stirred for 96 h at 100 °C. The solvent was evaporated in vacuo, ethyl acetate (100 mL) was added and the reaction was washed twice with water (100 mL). The layers were separated and the aqueous layer was acidified with concd HCl to pH 1. The resultant brown precipitate was filtered and placed in a Soxhlet extractor for 95 h (solvent: ethyl acetate). Evaporation of the solvent in vacuo gave 3,5-diphenylbenzoic acid as a light brown solid (0.512 g, 47%); mp 246 °C (Found: C, 82.92%, H, 5.11%. $C_{19}H_{14}O_2$ requires: C, 83.19%, H, 5.14%); ^1H NMR (200 MHz, $CDCl_3$): δ 7.44 (2H, m, ArH), 7.50 (4H, m, ArH), 7.67 (4H, m, ArH), 8.05 (1H, t, ^4J=1.8 Hz, ArH), 8.32 (2H, d, ^4J=1.8 Hz, ArH), 11.24

(1H, s, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 127.63, 128.03, 128.33, 129.34, 130.47, 131.52, 140.32, 142.63, 170.50 (CO_2); IR (DCM): ν_{max} 3062, 2820, 2658, 2592, 2520, 1694, 1597, 1504, 1468, 1437, 1402, 1339, 1292, 1265, 1243, 948, 894, 738, 699, 643 cm^{-1}; MS (MALDI-ToF): *m/z* 274 [M]$^+$, 229 [M$-CO_2H$]$^+$.

4.2.8. Silicon-phthalocyanine bis(3,5-diphenylbenzoate) (8). A mixture of 3,5-diphenylbenzoic acid (0.40 g, 1.64 mmol) and Si(Pc)Cl_2 (0.20 g, 0.33 mmol) was stirred in 2-methoxyethyl ether (20 mL) at 160 °C for 20 h. Workup as described for **1** gave **8** (0.10 g, 28%) as a bright blue solid; mp>400 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 6.68 (8H, m, ArH), 7.07 (12H, m, ArH), 7.54 (2H, m, ArH), 7.72 (2H, m, ArH), 8.28 (2H, m, ArH), 8.41 (8H, m, PcH), 9.74 (8H, m, PcH); ^{13}C NMR (125 MHz, $CDCl_3$) 124.55, 125.77, 126.65, 127.50, 128.75, 131.81, 135.89, 139.60, 140.44, 150.62, 159.70, 168.07 [all the Pc peaks and one ligand peak were not seen in ^{13}C NMR spectrum]; IR (DCM): ν_{max} 3050, 2362, 2340, 1390, 1270, 896, 746, 711 cm^{-1}; MS (MALDI-ToF): *m/z* 1086, 1087, 1088 [M]$^+$; HRMS found: 1086.3099, calcd for $C_{70}H_{42}N_8O_4Si$: 1086.3098.

4.2.9. Silicon-phthalocyanine bis(4-*tert*-butylphenoxide) (9). Sodium (4-*tert*-butyl)phenoxide (0.22 g, 1.27 mmol) and Si(Pc)Cl_2 (0.20 g, 0.33 mmol) were stirred together in 2-methoxyethyl ether (20 mL) at 160 °C for 11 h. Quenching of the reaction mixture in water (75 mL) followed by filtration of the resulting precipitate gave **9** as a blue solid (0.056 g, 20%); mp>400 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.56 (18H, s, CH_3), 2.35 (4H, d, ^3J=8.4 Hz, ArH), 5.53 (4H, d, ^3J=8.7 Hz, ArH), 8.32 (8H, m, PcH), 9.60 (8H, m, PcH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.88 (CH_3), 34.42 (*C*CH_3), 115.06 (ArH), 126.78 (ArH), 143.86 (ArH), 153.46 (ArH) [all the Pc peaks were not seen in the ^{13}C NMR spectrum]; IR (DCM): ν_{max} 3054, 2988, 2305, 1389, 1266, 896, 751, 707 cm^{-1}; MS (MALDI-ToF): *m/z* 838, 839, 840 [M]$^+$, 781, 782, 783 M$-^t$Bu]$^+$; HRMS found: 838.3200, calcd for $C_{52}H_{42}N_8O_2Si$: 838.3200.

4.2.10. Silicon-phthalocyanine bis(1-pyreneacetate) (10). 1-Pyreneacetic acid (510 mg, 1.96 mmol) and Si(Pc)Cl_2 (300 mg, 0.49 mmol) were stirred together in 2-methoxymethyl ether (3.0 mL) at 160 °C for 4 h. The solvent was removed in vacuo and the residue was filtered through a short silica gel column by eluting with DCM. The solvent was evaporated and the residue was chromatographed on silica gel using DCM as the eluent to afford compound **10** as a dark blue solid (160 mg, 32%); mp>400 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (4H, s, CH_2), 5.38 (2H, d, ^3J=7.8 Hz, pyrene), 5.52 (2H, d, ^3J=9.3 Hz, pyrene), 6.75 (2H, d, ^3J=7.8 Hz, pyrene), 6.79 (2H, d, ^3J=9.3 Hz, pyrene), 7.67 (2H, d, ^3J=8.8 Hz, pyrene), 7.92 (2H, d, ^3J=7.3 Hz, pyrene), 8.07 (2H, d, ^3J=9.3 Hz, pyrene), 8.09–8.16 (10H, m, PcH+pyrene), 8.31 (2H, d, ^3J=7.3 Hz, pyrene), 8.97 (8H, m, PcH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.68 (CH_2), 123.20 (PcH), 123.48, 123.66, 124.26, 124.67, 125.06, 125.45, 125.48, 126.32, 126.45, 126.89, 126.98, 127.58, 129.24, 130.43, 130.53, 131.35, 134.70, 149.12, 164.14 (CO_2); MS (MALDI-ToF): *m/z* 1058, 799.1, 800.1, 801.1 ([M$-$pyrene-CH_2CO_2]$^+$); HRMS found: 1058.2785, calcd for $C_{68}H_{38}N_8O_4Si$: 1058.2785.

4.2.11. Silicon-phthalocyanine bis(1-pyrenebutanoate) (11). 1-Pyrenebutyric acid (950 mg, 3.29 mmol) and Si(Pc)Cl_2 (500 mg, 0.82 mmol) were stirred together in 2-methoxymethyl ether (3.0 mL) under argon at 160 °C for 3 h. The solvent was removed in vacuo and the residue was filtered through a short silica gel column by eluting with DCM. The solvent was evaporated and the residue was chromatographed on a preparative silica gel TLC plate (2 mm thickness) using DCM as eluent to afford compound **11** (30 mg, 3%) as a dark blue solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ $-$0.50 (4H, t, ^3J=6.8 Hz, $CH_2CH_2\mathit{CH_2}CO_2$), $-$0.30 (4H, m, $CH_2\mathit{CH_2}CH_2CO_2$), 0.88 (4H, m, $\mathit{CH_2}CH_2CH_2CO_2$), 6.57 (2H, d, ^3J=7.8 Hz, pyrene), 7.12 (2H, d, ^3J=9.2 Hz, pyrene), 7.62 (2H, d, ^3J=7.8 Hz, pyrene), 7.68 (2H, d, ^3J=9.2 Hz, pyrene), 7.97 (2H, d, ^3J=7.8 Hz, pyrene), 7.99–8.18 (6H, m, pyrene), 8.24 (8H, m, PcH), 8.31 (2H, d, ^3J=7.8 Hz, pyrene), 9.56 (8H, m, PcH); MS (ES$^+$): *m/z* 1114.3, 1115.3, 1116.3 [M]$^+$; HRMS found: 1114.3412, calcd for $C_{72}H_{46}N_8O_4Si$: 1114.3411.

4.3. X-ray crystallography

The X-ray diffraction experiment was carried out on a Bruker SMART 3-circle diffractometer with an APEX CCD area detector, using a 60 W Mo-target microfocus Bede Microsource® X-ray generator with glass polycapillary X-ray optics (Mo Kα radiation, graphite monochromator, λ=0.71073 Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 cryostat. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL software (version 6.12, Bruker AXS, Madison WI, USA, 2001). Crystal data: $C_{44}H_{26}N_8O_4S_2Si$, **7**, M=822.94, T=120 K, monoclinic, space group $C2/c$ (no. 15), a=23.306(4), b=8.718(2), c=36.791(7) Å, β=107.98(1)°, V=7110(2) Å^3, Z=8, D_c=1.538 g cm^{-3}, μ=0.25 mm^{-1}, 22,658 reflections with $2\theta\leq50°$, R_{int}=0.129, final R=0.059 on 3556 reflections with $I\geq2\sigma(I)$, $wR(F^2)$=0.147 on all 6216 unique reflections. CCDC-290547.

4.4. UV–vis absorption 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 3-22 spectrofluorimeter or a Spex Fluoromax 2 spectrofluorimeter and were corrected for the spectral response of the machine. Lifetimes were recorded using the technique of time correlated single photon counting.[19,26] Quantum yields were determined by the comparative method of Williams et al.,[27] measurements being taken using several dilutions of each sample to negate concentration effects. Disulfonated aluminium Pc (Φ_f= 0.40) was used as the standard.

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