Use of Piers–Rubinsztajn Chemistry to Access Unique and Challenging Silicon Phthalocyanines

Anjuli M. Szawiola, Benoit H. Lessard, Hasan Raboui, and Timothy P. Bender*

ABSTRACT: Axial functionalization is one mode that enables the solubility of silicon phthalocyanines (SiPcs). Our group observed that the use of typical axial functionalization methodologies on reaction of Cl₂SiPc with the chlorotriphenyl silane reagent unexpectedly resulted in the equal formation of triphenyl silyloxy silicon tetrabenzotriazacorrole ((3PS)-SiTbc) and the desired bis(tri-phenyl siloxy)-silicon phthalocyanine ((3PS)₂-SiPc). The formation of a (3PS)-SiTbc was unexpected, and the separation of (3PS)-SiTbc and (3PS)₂-SiPc was difficult. Therefore, in this study, we investigated the use of Piers–Rubinsztajn (PR) chemistry as an alternative method to functionalize the axial position of a SiPc to avoid the generation of a Tbc derivative. PR chemistry is a novel method to form a Si−O bond starting with a Si−H-based reactant and a −OH-based nucleophile enabled by tris(pentafluorophenyl)borane as a catalyst. The PR chemistry was screened on several fronts on how it can be applied to SiPcs. It was found that the process needs to be run in nitrobenzene at a molar ratio and at a particular temperature. To this end, the triphenylsiloxy derivative (3PS)₂-SiPc was produced and fully characterized, without the production of a Tbc derivative. In addition, we explored and outlined that the PR chemistry method can enable the formation of other SiPc derivatives that are inaccessible utilizing other established axial substitution chemistry methods such as (TM₃)₂-SiPc and (MDM)₂-SiPc. These additional materials were also physically characterized. The main conclusion is that the PR chemistry method can be applied to SiPcs and yield several alternative derivatives and has the potential to apply to additional macrocyclic compounds for unique derivative formation.

INTRODUCTION

Phthalocyanines (Pcs) are a class of materials consisting of four (4) imine-linked isoindole subunits that are used as stable dyes and pigments due to their high absorption coefficient. They form coordination complexes with almost every single metal in the periodic table. Their 18 π-electron, macrocyclic, planar structure provides an interesting variety of physical, electrochemical, and optoelectronic properties, including their ability to absorb visible light.¹

Silicon phthalocyanines (Figure 1, SiPcs) have a good history within the dye and pigment space but have recently emerged to be of general interest for organic electronic applications due to their optoelectronic properties and the relative abundance of silicon. SiPcs have been applied in a variety of organic electronic devices, including organic light-emitting diodes,²⁻⁴ organic thin-film transistors,⁵ planar heterojunction organic photovoltaics,⁶ bulk heterojunction organic photovoltaics as both electron acceptors/conductors and ternary additives,⁷⁻¹⁰ and dye-sensitized solar cells.¹¹⁻¹⁷

Axial functionalization is one manner of modifying a subset of phthalocyanines (Pcs) with coordinated metallic atoms having additional atomic bonding options. The bonding options can enable a Pc to transition from a pigment status to the dye status and can enable significant variations. Specifically, for organic electronics applications, SiPcs require variations of axial functionalization to enable different morphological, nanostructural, and physical properties including solubility,²¹,²² while leaving their desired optoelectronic properties intact. For example, (HO)₂-SiPcs and Cl₂-SiPcs have been modified by the use of various chlorosilane derivatives²¹,²³ and react with alcohols at reflux to make alternative axial substituents non-silicon-based.²⁴⁻²⁶ Each approach valid to access a variety of SiPc products yet is a limitation when it comes to axial substituents for the SiPcs. This approach and requirements are also analogous to what has also been employed within boron subphthalocyanine (BsubPc) derivatives to also enable varying physical and nanostructural properties.²⁶

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The general mechanism for the formation of a Pc is the reaction of a phthalonitrile precursor (which can have peripheral substituents) with the associated metallic source in a halogenated form to enable the metallic source to be a Lewis acid. The relative Lewis acidity of the metallic source to the Pc. Short of the Lewis basicity and acidity being a factor, the actual mechanism of the formation of a Pc is not established to date. SiCl₄ has low Lewis acidity; therefore, to form a SiPc, the standard need is to react 1,3-diaminoisoindoline (1,3-DII) with SiCl₄ at high temperature (Figure 1, point i). 1,3-DII is an alternative to and a derivative of phthalonitrile needed when the metallic source of a Pc has a low Lewis acid (such as SiCl₄). 1,3-DII is derived from a phthalonitrile on reaction with NaOCH₃ on reflux in methanol and bubbling ammonia (NH₃) through the reactor.²⁷ 1,3-DII ultimately has a higher Lewis basicity due to its nitrogen atomic features and therefore enables the formation of Cl₂-SiPc on reaction with SiCl₄. Cl₂-SiPc has low solubility and is a pigment, and its crystal structure has been established.²⁸,²⁹

One more specific method used for axial functionalization of SiPcs involves first the formation of (HO)₂-SiPc on hydration of Cl₂-SiPc (Figure 1, point iii). The reaction of chloro-tri(alkyl/aryl) silane with (HO)₂-SiPc in pyridine at reflux under an inert atmosphere then enables the axial substituent and the associated physical properties to vary (Figure 1, point iv).³⁵,³⁶ This method is (relatively) limited by the availability of chloro-tri(alkyl/aryl) silane derivatives and is relatively simple chemistry with a HCl/pyridine-HCl byproduct.

The stimulation of this report resulted from our attempt to synthesize bis(tri-phenyl siloxy)-silicon phthalocyanine (3PS)₂-SiPc using this methodology, the reaction of (HO)₂-SiPc with an excess of chloro-triphenylsilane in refluxing pyridine (Figure 1, point iv). The unexpected results we observed was a mixture of both the desired product (3PS)₂-SiPc and an unexpected side product. Each product was isolated by train sublimation.³⁰ We observed that the product remaining in the boat (~50%) had a different appearance from the material that sublime and traveled down the tube (~50%). We characterized both the product in the boat and the product that sublime first by UV–vis absorption spectroscopy (Figure 2a, a direct point of comparison, (3HS)₂-SiPc¹⁰ is included). The product that was sublime has two characteristic peaks which are similar to those of (3HS)₂-SiPc (636 and 675 nm), while the product that was left in the boat contains a similar absorption profile and has an additional absorption at 443 nm (Figure 2b). This new peak is consistent and characteristic of a ring-contracted SiPc macrocycle, as has been reported by Zhang et al.,³¹,³² Kobayashi et al.,³³,³⁴ and Raboui et al.,³⁴,³⁵ forming a compound known as a tetrabenzo-triazacorrole (Tbc, Figure 1), a ring-contraction Pc analogue; in this case, (tri-phenyl)phthalonitrile tetrabenzo-triazacorrole (3PS-Tbc, Figure 2).

Figure 1. Generic structures of a silicon Pc (SiPc) with axial functionalization (X). (a) Process to make an axial functionalized SiPc: (i) reaction of SiCl₄ with 1,3-diaminoisoindoline (1,3-DII) in quinoline as a solvent for approximately 4 h at a refluxing temperature of 219 °C under an inert N₂ (g) atmosphere; (ii) then, on the formation of Cl₂-SiPc, axial functionalization can occur (axial substituents shown as X) on reaction with a chloro trialkyl/aryl silane in the presence of sodium hydroxide and Aliquat phase catalysis at a refluxing temperature of 132 °C in chlorobenzene for 2–3 h and is called the “AQ” method; (iii) an alternative pathway is to hydrolyze the Cl₂-SiPc to (HO)₂-SiPc and (iv) react (HO)₂-SiPc also with chloro trialkyl/aryl silanes at a refluxing temperature of 115 °C in pyridine for ~5 h and is called the “BG” method; (v) to specifically form a silicon tetrabenzo-triazacorrole (SiTbc; unique C==C highlighted in pink), (HO)₂-SiPc is reacted with a chloro trialkyl/aryl silane at 100 °C in pyridine in the presence of magnesium (Mg). (b) 3D crystal molecular structures of (3PS)₂-SiPc (top, CCDC deposition number:1824908; database identifier GICYAV) and 3PS-SiTbc (bottom, CCDC deposition number: 1817928; database identifier KICMIV; unique C==C bond highlighted in pink), where 3PS is triphenyl siloxane. Carbon—gray; nitrogen—blue; silicon—yellow; oxygen—red. On the formation of Cl₂-SiPc, axial substitution can proceed with a mixture of reagents of chloro trialkyl/aryl silane, sodium hydroxide, potassium carbonate, and an Aliquat phase-transfer catalyst for refluxing in chlorobenzene (Figure 1, point ii) and presumably forms (HO)₂-SiPc in situ due to the use of sodium hydroxide and an Aliquat,²⁷ and (HO)₂-SiPc reacts with the chloro trialkyl/aryl silane.
Table 1. Scoping Conditions Explored for the PR Reaction$^{a}$

| solvent            | calculated Hammett parameter | catalyst dose 1 | catalyst dose 2 | temperature (°C) | reaction result$^{b}$ |
|--------------------|------------------------------|----------------|----------------|------------------|-----------------------|
| toluene            | $-0.170$                     | 5 mol %        |                | 100              | (−)                   |
|                    |                              |                | 5 mol %        | 100              | (−)                   |
|                    |                              |                |                | 25               | (−)                   |
| 1,2-dichlorobenzene| $0.454$                      | 5 mol %        |                | 100              | (−)                   |
|                    |                              |                | 5 mol %        | 25               | (−)                   |
|                    |                              |                |                | (−)              |                       |
| chlorobenzene      | $0.227$                      | 5 mol %        |                | 100              | (−)                   |
|                    |                              |                | 5 mol %        | 25               | (−)                   |
|                    |                              |                |                | (−)              |                       |
| nitrobenzene       | $0.778$                      | 5 mol %        |                | 100              | (−)                   |
|                    |                              |                | 5 mol %        | 100              | (+)                   |
|                    |                              |                |                | 25               | (−)                   |
| dicloromethane     |                              | 5 mol %        |                | 100              | (−)                   |
|                    |                              |                | 5 mol %        | 25               | (−)                   |
| xylenes            | $-0.247$                     | 5 mol %        |                | 100              | (−)                   |

$^{a}$(−)—No axial substituted bis(tri-n-hexylsilyl oxide) silicon phthalocyanine, (3HS)$_2$-SiPc, formed; (o)—modest axial substituted (3HS)$_2$-SiPc formed; (+)—full functionalization axial substitute (3HS)$_2$-SiPc achieved. $^{b}$ (o) denotes a partially positive result.
in pyridine at reflux, with Mg being a requirement for complete conversion (Figure 1, point v). As Mg has a major impact, maybe it is not fully required for the formation of a SiTbc. Rather, as this reaction was held, it would generate HCl on reaction of (HO)2-SiPc with chloro-triphenylsilane (Figure 2), and therefore, the potential presence of pyridine-HCl during the reaction is a factor into the formation of SiTbcs.

We then considered how we might synthesize (3PS)2-SiPc without the significant formation of a Tbc. Piers–Rubinsztajn (PR) chemistry is one method to be considered. We have previously demonstrated the use of PR chemistry in coupling triarylamines to siloxane oligomers or polymers for the generation of new materials.39–44 This type of chemistry has also been used to make many other functional materials such as siloxane-based foams,45,46 surfactants,47 cross-linkers with other unique cyclic macrocycles.62 The PR reaction uses various aromatic solvents, the number of catalyst doses, and temperature on the PR reaction process.

To expand the scope of this reaction, it was hypothesized that the PR reaction could be used to (1) eliminate the formation of a Tbc when synthesizing the triphenyl derivatized SiPc and additionally (2) access unique, non-chlorosilane derivatives (i.e., siloxane oligomer derivatives). The goal of this study was to do determine the feasibility of using the PR reaction specifically with the starting material (HO)2-SiPc yielding silyloxo-SiPcs, a broad class of SiPcs with high solubility that enables several unique applications as outlined above and can enable unique derivatives that are relevant to the field. We do also compare two other methods, the “BG” and “AQ” methods (outlined below), as for these, they will generate pyridine-HCl during reaction.

### RESULTS AND DISCUSSION

**Reaction Scoping.** As outlined above, the intention of this work had two goals: (1) to establish the PR reaction to functionalize SiPcs, without the generation of the Tbc side product and (2) to access unique SiPc derivatives. To start, the PR reaction was scoped to access its potential for functionalizing SiPcs. To enable relative easy scoping/assessment, we used a molecular fragment known to give outstanding solubility: tri-n-hexylsilsilane (3HS), a derivative that would yield bis(tri-n-hexylsiloxyl oxide)silicon phthalocyanine, (3HS)2-SiPc.9,10,14,16,66,67 In this case, the Si–H bond was in tri-n-hexylsilane, the nucleophile was the hydroxyl group attached to the (HO)2-SiPc, and the volatile gas released was hydrogen (H2) gas (caution).

The impact of a variety of solvents, the number of catalyst doses, and temperature on reaction progress was investigated and is outlined in Table 1. The different solvents chosen for this reaction were to scope common organic solvents that were inert to this reaction. The number of catalyst doses (i.e., one or two) was also investigated to ensure the presence of a sufficient amount of catalyst during the reaction. Since previous work demonstrated the ability of triarylamines to be functionalized by the PR reaction at 25 °C,44 this temperature was selected to be studied for SiPc functionalization as well. The reaction rate at a higher temperature of 100 °C was also studied to assess temperature dependence on the PR reaction process.

Thin-layer chromatography (TLC) analysis was used to monitor the reaction progress with a solvent system of 1:1 hexanes/tetrahydrofuran (THF). The starting material, (HO)2-SiPc, has poor solubility in the TLC solvent system and adheres to the base of the TLC system, while the functionalized SiPc, (3HS)2-SiPc, is very soluble and has high TLC mobility, and the intermediate (3HS)-Cl-SiPc has modest solubility and mobility on a TLC. The reaction progress can be visualized by the intensity under visible light, relevant to the starting material spot at the baseline. On exploration of a significant matrix (Table 1), it was discovered that the conditions that led to complete conversion of the starting material were as follows: nitrobenzene, with two 5 mol % catalytic doses and a temperature of 100 °C over 6 h time. This result gave positive confirmation that the PR reaction could indeed be used to functionalize SiPcs.

In retrospect, it is not surprising that nitrobenzene is the best solvent based on a Hammett parameter assessment (Table 1). The Hammett parameter values can be summarized from a review by Hansch.38 Nitrobenzene has the highest positive Hammett parameter, indicating its π-acidity relative to the other aromatic solvents. Past results focusing on triarylamines44 and polysiloxane derivatization44 worked well in toluene and xylenes, respectively. However, the π-acidity of toluene and xylene relative to nitrobenzene is clearly a factor here whereby the molecular level interactions between nitrobenzene and tris(pentafluorophenyl)borane would be far less favorable (two π-acidic/Lewis-acidic materials). These results likely then set a parameter for less reactive nucleophilic species in the PR process to use a π-acidic solvent. The presumed low nucleophilicity of (HO)2-SiPc is likely attributable to the steric effect of its molecular size and positioning of the −OH group. In this process, nitrobenzene is also able to effectively solubilize all three reagents, thereby making it the solvent of choice moving forward.

**Synthesis of (3PS)2-SiPc via the PR Methodology.** After having confirmed PR chemistry as a viable means to functionalize SiPcs, one of the initial goals of using PR chemistry with SiPcs (as stated above) is to eliminate the formation of Tbcs while working to obtain certain derivatives. The PR methodology outlined above was then applied to generate the desired bis(tri-phenyl siloxy)-silicon phthalocyanine (3PS)2-SiPc. This methodology worked and did not generate the undesired Tbc derivative, as confirmed by UV–vis absorption spectroscopy (Figure 3) and other characterization techniques [nuclear magnetic resonance (NMR), Figures S1, S8.5; mass spectrometry, Figure S2, S8.10]. This is therefore the first confirmation of the uniqueness of the PR methodology, which can be applied to Pcs and target unique and desirable derivatives.

The absorption spectrum of (3PS)2-SiPc has a strong Q-band transition at 676 nm and a Soret band transition at ~350 nm, typical and characteristic of Pcs. Interestingly, the Q-band transition is red-shifted 8 nm as compared to a literature value for this compound obtained in toluene (668 nm21), demonstrating a potential solvatochromic effect. Figure 3 also shows the photoluminescence (PL) spectra of this compound at different excitation wavelengths. The PL excitation wavelengths were selected as the absorbance peaks in the UV–vis absorbance spectrum (350, 610, 650, and 670 nm). The material retains the same PL profile and thus the structure, regardless of the excitation wavelength. In addition, a Stokes shift of ~10 nm can be observed. The Stokes shift, as
Based on the thermal analysis, (3PS)\textsubscript{2}-SiPc has a higher calorimetry (TGA/DSC), Figures S3 and S4 was conducted. This is confirmed by higher enthalpy of crystallization and melting values. (3PS)\textsubscript{2}-SiPc also has a higher 5\% weight loss temperature than the 3BS derivatives, of this compound, such that its maximum emission wavelength is 6 nm red-shifted as compared to that in toluene.

To study the material morphology in detail, a thermal analysis [thermal gravimetric analysis/differential scanning calorimetry (TGA/DSC), Figures S3 and S4] was conducted. Based on the thermal analysis, (3PS)\textsubscript{2}-SiPc has a higher \( T_c \) and \( T_m \) than those observed with an alkyl derivative, for example, the bis(tri-butyl siloxy) SiPc derivative, (3BS)\textsubscript{2}SiPc.\textsuperscript{16} This would indicate a higher degree of structure and order to the solid state. This is confirmed by higher enthalpy of crystallization and melting values. (3PS)\textsubscript{2}-SiPc also has a higher 5\% weight loss temperature than the 3BS derivatives, indicating a higher thermal stability.

As SiPcs are relevant to organic electronic applications, electrochemistry was also explored. Half-wave potentials, \( E_{\text{red}} \) and \( E_{\text{ox}} \), for (3PS)\textsubscript{2}-SiPc were also obtained via cyclic voltammetry (CV, Table 2, Figure S5) and were found to be typical of SiPc derivatives\textsuperscript{10,20} and are also consistent with the previously reported values for (3PS)\textsubscript{2}-SiPc, within 15 mV for both the oxidation and reduction potentials.

**Other Derivatives via the PR Methodology.** We then explored the PR methodology to enable the use of unique commercially available siloxane oligomers with silane-derivative points, which are unavailable as chlorosilanes analogues to yield unique SiPc derivatives with siloxane oligomers in the axial position. The examples we considered were bis(tris(trimethylsiloxy)silyl oxide) silicon phthalocyanine, (TM\textsubscript{3})\textsubscript{2}-SiPc, and bis(bis(trimethylsiloxy)methyl silyl oxide) silicon phthalocyanine, (MDM\textsubscript{2})-SiPc (outlined in Scheme 1). With regard to the generation of (TM\textsubscript{3})\textsubscript{2}-SiPc, using the PR method outlined above, upon MS characterization, it was found that there was a mixture of compounds, including a minor amount of a Tbc derivative, resulting from the (TM\textsubscript{3})\textsubscript{2}-SiPc sample (Figure S6). The product mixture resulting from the MS analysis also contained a variety of different axially functionalized siloxane derivatives. It would appear that a significant amount of metathesis occurred among the TM\textsubscript{3} molecular fragment on MS characterization. It should be noted, however, that a UV–vis spectrum of the mixture of compounds did not indicate Tbc formation by the lack of the characteristic peak of a Tbc at \( \sim 440 \) nm (Figure 4). This therefore indicates the possibility of Tbc formation only during the MS technique. Therefore, this is to note that the formation of Tbcs may occur via varying ways of analysis and under varying analytical conditions. However, NMR analysis (Figure S7) also firmly indicated the lack of Tbc formation during the synthetic process. Three separate Pc-species peaks were observed, and more –O–Si–C–H protons (\( \sim 84 \) H) than would be expected of a tris(trimethylsiloxy)silane on a difunctional SiPc (54 H) were observed, thus confirming a mixture of products.

The reduction and oxidation potentials of (TM\textsubscript{3})\textsubscript{2}-SiPc are similar to those observed with (3PS)\textsubscript{2}-SiPc (Figure S5, Table 3); however, the reduction potential here is irreversible, indicating the inability to oxidize the reduced sample back to neutral as a result of an electrochemical reaction. The lack of a crystallization or melting temperature in the thermal analysis is due to the flexibility, variation, and the rotational nature of the siloxane groups. The absorption spectrum (Figure 4) shows a strong Q-band transition at 670 nm and a Soret band transition at \( \sim 440 \) nm, characteristic of Pcs. Figure 4 also shows the PL spectra of this compound at different excitation wavelengths. The PL excitation wavelengths were selected as the absorbance peaks in the UV–vis absorbance spectrum (350, 610, 650, and 670 nm), the same as those used with the (3PS)\textsubscript{2}-SiPc derivative. The material retains the same PL profile and thus the structure, regardless of the excitation.

**Table 2. Characterization Results of the Compound (3PS)\textsubscript{2}-SiPc**

| Characteristic | (3PS)\textsubscript{2}SiPc via PR chemistry | (3PS)\textsubscript{2}SiPc literature values |
|---------------|--------------------------------------------|---------------------------------------------|
| \( E_{\text{red}} \) (vs Ag/AgCl) | –0.82 V | –0.88 (versus SCE)\textsuperscript{37} |
| \( E_{\text{ox}} \) (vs Ag/AgCl) | 1.01 V | –0.835 V (versus Ag/AgCl)\textsuperscript{37} |
| \( T_{5\%} \) | 395 °C | 0.95 V (versus SCE)\textsuperscript{37} or 0.995 V (versus Ag/AgCl)\textsuperscript{49} |
| \( \Delta H_{5\%} \) | 59.7 J/g | 668 nm (toluene)\textsuperscript{35} |
| \( \lambda_{\text{max, vis, solution}} \) | 676 nm (DCM) | 672 nm (toluene)\textsuperscript{35} |
| \( \lambda_{\text{max, PL, solution}} \) | 686 nm (DCM) | |

\textsuperscript{37}Converted to Ag/AgCl by adding 0.045 V versus SCE values.
wavelength. In addition, a Stokes shift of \( \sim 15 \text{ nm} \) can be observed.

Bis(bis(trimethylsiloxy)methyl silyl oxide) silicon Pc \[(\text{MDM})_2\text{-SiPc}, \text{Scheme 1}\]\ was also synthesized, but it was found that the thermal stability of this material was limited as its TGA profile (Figure S3) showed an uneven decline in mass above \( \sim 160 \text{ °C} \), which could be associated with material decomposition \( (T_{d,5\%} = 161 \text{ °C}) \). In comparison, the TGA profiles of \((3\text{PS})_2\text{-SiPc}\) and \((\text{TM}_3)_2\text{-SiPc}\) have a sharp decrease in weight loss, associated with material decomposition/sublimation. Therefore, due to the decreased thermal stability of \((\text{MDM})_2\text{-SiPc}\), it could not be purified through sublimation; thus, it could not be appropriately characterized via NMR, MS, PL, or electrochemistry to consider its organic electronic application. However, this did show the flexibility of the PR synthesis method and highlights some points to consider from a synthetic methodology point of view.

**Evaluation of the PR Methodology via Direct Points of Comparison.** While PR chemistry certainly can be applied to achieve siloxane and other axial derivatives of SiPcs, it was desirable to evaluate the PR methodology against other available methods for the axial functionalizing of SiPcs yielding silyloxy-SiPc derivatives that have been reported in the literature and patents and verified within our laboratory (Scheme 2). The goal was to report a process/chemistry choice of obtaining SiPc axial substituents based on the availability of the reagents for the axial substitution. The PR process outlined above and concluded will be referred to as the "PR" method in this section. The additional two methods that were investigated for points of comparison to PR chemistry were the so-called "Benoit-Grant (BG)" \(^{21}\) and "Aliquat (AQ)" \(^{23}\) methods. The "BG" method (Scheme 2) involves the reaction of a chloro-trialkyl/aryl silane with \((\text{HO})_2\text{-SiPc}\) in pyridine at reflux. \(^{21}\) The \((\text{HO})_2\text{-SiPc}\) precursor is generated via reaction of \(\text{Cl}_3\text{-SiPc}\) with a nucleophilic \(\text{−OH}\) source which was developed as basic hydrolysis does not work for SiPc derivatives. The "AQ" method uses \(\text{Cl}_3\text{-SiPc}\) as the starting material; circumvents the need to generate \((\text{HO})_2\text{-SiPc}\) in pyridine; and presumably forms \((\text{HO})_2\text{-SiPc}\) in situ. \(^{23}\)

As above, the trihexyl SiPc derivative \((3\text{HS})_2\text{-SiPc}\) was targeted with each process to compare the yields of the three methods as the chloro and hydride derivative of trihexyl-silane is equally available. This derivative was also chosen as highly...
Scheme 2. (i) SiCl₄, Quinoline, 4 h, 219 °C, under N₂ (g); (ii) CsOH (50 wt % in H₂O), DMF, 120 °C, 4 h under Ar; (g) (iii) “BG” Method—Chlorotri-n-butylsilane, Pyridine, 115 °C, 5 h under Ar (g); (iv) “PR” Method—Tri-n-butylsilane, B(C₆F₅)₃, Nitrobenzene, 22 h under Ar; (v) “AQ” Method—Chlorotri-n-hexylsilane, Sodium Hydroxide, Aliquat HTA-1, Potassium Carbonate, Chlorobenzene, 132 °C under Ar

Table 4. Summary of Yields of (3HS)₂-SiPc Samples

|       | 3HS | AQ | BG | PR |
|-------|-----|----|----|----|
| crude yield | 81% (4.32 g) | 23% (0.868 g) | 74% (0.733 g) |    |
| sublimation yield | 80% (0.404 g) | 50% (0.154 g) | 83% (0.251 g) |    |

“Crude yield is based on reaction. Sublimation went forward and may not have used 100% of the crude; therefore, the percentage (%) yield on sublimation and the mass (g) outlined are based on alternative amounts of crude going forward with sublimation.

Table 5. Summary of Yields and Properties of (3BS)₂-SiPc Samples

|       | 3BS | AQ | BG | PR |
|-------|-----|----|----|----|
| crude yield | 57% (2.61 g) |     | 81% (1.69 g) | <50% (0.86 g) |
| sublimation yield | 91% (0.29 g) |     | 59% (0.2 g) | 48% (0.139 g) |
| ΔTₐ, % | 293 °C |     | 281 °C | 289 °C |
| ΔHₐ/ΔHₛ₂ (J/g) | 63 °C/234 °C |     | 63 °C/234 °C | 63 °C/234 °C |
| ΔTₛ₁/ΔTₛ₂ | 29.7/40.4 |     | 35.4/23.7 | 38.6/38.6 |
| ΔHₛ₁/ΔHₛ₂ (J/g) | 63 °C/212 °C |     | 61 °C/200 °C | 62 °C/196 °C |
|                | 25.6/44.2 |     | 33.5/38.6 | 33.9/39.4 |
sublimation. This indicates that in both cases with 3HS and 3BS, the AQ method produces a higher-purity material over the BG and PR methods. Additionally, it can be surmised that the yield of the PR method depends on the solubility of the derivative (3HS more soluble than 3BS).

The thermal properties of these three samples were studied to examine the effect of the synthetic process on morphology. The TGA results (Figure 5a) reveal different % mass loss temperatures ($T_{d,5\%}$). The AQ sample is modestly most thermally stable, closely followed by the PR and then BG samples. All three compounds have virtually identical degradation profiles.

The DSC results (Figure 5b,c) yield additional information on the melting and crystallization properties of these SiPc derivatives, including their melting temperature ($T_m$), crystallization temperature ($T_c$), enthalpy of melting ($\Delta H_m$), and enthalpy of crystallization ($\Delta H_c$). The enthalpy values were obtained by integrating the DSC traces at the identified temperatures. For all three compounds, two melt/crystallization transitions were observed. The first transition occurred at approximately 63 °C and was consistent between heating and cooling curves across all three compounds. The enthalpies associated with this transition point were also very similar in each series but slightly different across the series ($AQ - \Delta H_{m,1} \approx 36 J/g$, $BG - \Delta H_{c,1} \approx 34 J/g$, $PR - \Delta H_{c,1} \approx 36 J/g$).

The second transition temperature was more varied between heating and cooling curves across all series (ranging as much as 38 °C in the PR series between heating and cooling curves), indicating a path-dependent (i.e., heating vs cooling) effect on the melting transition. The enthalpies associated with this transition point were similar in AQ and PR series but widely differing for BG ($AQ - \Delta H_{m,2} \approx 42 J/g$, $BG - \Delta H_{m,2} \approx 42 J/g$ & $\Delta H_{m,2} \approx 24 J/g$, $PR - \Delta H_{m,2} \approx 39 J/g$). The disparity observed with BG can possibly be explained by potential impurities present in the sample or structural defects, thus lowering the energy required for a melt transition, at elevated temperatures.

Based on this thermal characterization study, the PR method generates a batch of (3BS)$_2$SiPcs that is very similar to batches generated by the other two methods and thus can be considered a comparable method for SiPc functionalization. The main differences being observed between the three batches were in their enthalpies and second crystallization temperatures.

**CONCLUSIONS**

This study outlines the first ever use of PR chemistry to axially functionalize a silicon phthalocyanine (SiPc). This method has been shown to be applicable to a variety of alkyl/aryl axial substituent derivatives, without the byproduct formation of a Tbc derivative. The triphenylsilane derivative, (3PS)$_2$-SiPc, being the first example was synthesized and characterized by CV, TGA/DSC, NMR, MS, UV—vis, and PL spectroscopy.

In addition, PR chemistry has been shown here to enable the synthesis of siloxane-functionalized derivatives via commercially available silanes. However, the synthesis of a tris-(trimethylsiloxy) derivative, (TM$_3$)$_2$-SiPc, resulted in a mixture of products and the synthesis of a bis(dimethylsiloxy)methyl derivative. Now, this mixture formed was not clear but is just an observation to note. The formation of (MDM)$_2$-SiPc, was successful; the compound was however thermally unstable and unable to be purified and is just another observation to note as one considers the PR process for Pc derivatives.

A PR process-derived SiPc was also compared against two other SiPc functionalization methods (BG and AQ). The comparison demonstrated that the PR reaction is capable of synthesizing a derivative that has very similar thermal characteristics to the same derivative synthesized via the two other methods. This ascertains PR chemistry as a viable means to functionalize SiPcs. This also brings out the hidden potential of PR chemistry to access certain Pc products/derivatives that are whether derivatives that have been previously obtainable by alternative processes or derivatives that are now only accessible via the PR method.

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**Figure 5.** (a) TGA trace of three (3BS)$_2$SiPc compounds synthesized by different methods; (b) DSC trace of all three (3BS)$_2$SiPc samples on the first cooling ramp of a heat/cool/heat cycle; (c) DSC trace of all three (3BS)$_2$SiPc samples on the second heating ramp of a heat/cool/heat cycle.
**EXPERIMENTAL SECTION**

**Materials.** All materials were obtained from Sigma-Aldrich, except 1,3-diminoisoindoline, which was obtained from Xerox Corp. (Mississauga, ON, Canada). Chlorotri-n-hexylsilane, chlorotri-n-butylsilane, tri-n-hexylsilane, tri-n-butylsilane, and triphenylsilane were obtained from Gelest, Inc. (Pennsylvania, USA), and tris(pentaphenylfluoroborate) was obtained from Strem Inc. (Massachusetts, USA). Solvents were obtained from Caledon (Caledon, Ontario, Canada). All materials were used as received without further purification.

TLC was performed on aluminum plates coated with silica (a pore size of 60 Å) and a fluorescent indicator, obtained from Whatman Ltd., and visualized under UV (254 nm) light.

**Dichloro-Silicon Phthalocyanine (Cl₂-SiPc).** Cl₂-SiPc was synthesized according to the literature. For example, to an oven-dried three-neck round-bottom flask were added 1,3-diminoisoindoline (12.00 g, 0.082 mol) and quinoline (94.6 mL). The mixture was heated to 50 °C for 15 min under N₂, and then, SiCl₄ (9.46 mL, 0.082 mol) was added via a syringe. The reaction mixture was then heated to 219 °C for 4 h. The reaction mixture was then cooled to 185 °C and vacuum-filtered hot. The residue was then washed with 50 mL of quinoline, 150 mL of toluene, 250 mL of methanol, and 150 mL of acetone. The material was vacuum-oven-dried overnight at 80 °C to yield a shiny purple powder (crude yield = 82%).

**Bis(hexyloxy)-Silicon Phthalocyanine (HO)₂-SiPc.** (HO)₂-SiPc was synthesized according to the literature. To an oven-dried three-neck round-bottom flask were added Cl₂-SiPc (2.5 g, 4.09 mmol), dimethylformamide (25 mL), and cesium hydroxide (50 wt % solution in H₂O) (1.50 g, 10.0 mmol) under argon. The reaction mixture was heated to 120 °C for 10 h. The crude product was precipitated into methanol and filtered to give a dark-blue powder (crude yield = 94%), which was used without further purification. LRMS (EI) m/z: [M] calcd for 1092.32; found, 1092.3. ¹HNMR (500 MHz, C₆D₆): δ 9.45 ppm (8 H, s), 8.29 (8 H, s), 6.68 (6 H, m), 6.28 (12 H, m), 4.78 (12 H, m).

**Bis((bis(trimethylsiloxy)methyl) Silyl Oxide) Silicon Phthalocyanine, (TMH)₂-SiPc.** To an oven-dried pressure vessel flask were added (HO)₂-SiPc (0.3 g, 0.52 mmol) and nitrobenzene (17 mL). Argon gas was bubbled through the solution for 2 min. Tri(hexyloxy)silane (1.55 g, 5.2 mmol) and tris(pentaphenylfluoroborate) (18.9 mg, 0.037 mmol) via the stock solution were added, and the vessel was submerged into an oil bath at 100 °C. A dose of 18.9 mg of tris(pentaphenylfluoroborate) (via the stock solution) and 1.55 g of tri(hexyloxy)silane were added after 2.5 h and 7.5 h of reaction time. The reaction was monitored via silica TLC plates using a 1:1 hexanes/THF system. The reaction was then left for an additional 15 h before cooling to room temperature. The solution was then rotovapped to dryness. The solid was then collected and dried in a vacuum oven overnight at 80 °C to yield a dark-blue powder (crude yield = 80%). The material was purified via train sublimation prior to use. LRMS (EI) m/z: [M] calcd for 1092.32; found, 1092.3. ¹HNMR (500 MHz, CDCl₃): δ 9.77 ppm (4 H, q), 9.74 (8 H, q), 9.71 (8 H, q), 7.96 (4 H, q), 7.93 (4 H, q), 7.91 (4 H, q), −0.91 (m, 42 H), −0.97 (m, 42 H).

**Bis((bis(trimethylsiloxy)methyl) Silyl Oxide) Silicon Phthalocyanine, (MDM)₂-SiPc.** To an oven-dried pressure vessel flask were added (HO)₂-SiPc (0.3 g, 0.52 mmol) and nitrobenzene (17 mL). Argon gas was bubbled through the solution for 2 min. Bis(hexyloxy)silane (1.17 g, 5.2 mmol) and tris(pentaphenylfluoroborate) (18.9 mg, 0.037 mmol) via the stock solution were added, and the vessel was submerged into an oil bath at 100 °C. A dose of 18.9 mg of tris(pentaphenylfluoroborate) (via the stock solution) and 1.55 g of bis(hexyloxy)silane were added after 2.5, 5, and 7.5 h of reaction time. The reaction was monitored via silica TLC plates using a 1:1 hexanes/THF system. The reaction was then left for an additional 15 h before cooling to room temperature. The solution was then rotovapped to dryness. The solid was then collected and dried in a vacuum oven overnight at 80 °C to yield a dark-blue powder (crude yield = 84%). The material was purified via train sublimation prior to use. LRMS (EI) m/z: [M] calcd for 1092.32; found, 1092.3. ¹HNMR (500 MHz, C₆D₆): δ 9.77 ppm (4 H, q), 9.74 (8 H, q), 9.71 (8 H, q), 7.96 (4 H, q), 7.93 (4 H, q), 7.91 (4 H, q), −0.91 (m, 42 H), −0.97 (m, 42 H).

**Bis((tri-n-hexyl Silyl Oxide) Silicon Phthalocyanine, (PR) Method, PR-(3HS)₂-SiPc.** To an oven-dried pressure vessel vessel were added (HO)₂-SiPc (0.5 g, 0.86 mmol) and nitrobenzene (28 mL). Argon gas was bubbled through the solution for 2 min. Tri-n-hexylsilane (2.41 g, 8.63 mmol) and tris(pentaphenylfluoroborate) (30.7 mg, 0.06 mmol) via the stock solution were added, and the vessel was submerged into an oil bath at 100 °C. A dose of 30.7 mg of tris(pentaphenylfluoroborate) (via the stock solution) and 2.41 g of tri-n-hexylsilane were added after 2.5 h and 5 h of reaction time. The reaction progress was monitored via silica TLC plates using a 1:1 hexanes/THF system. The reaction was then cooled to room temperature. Nitrobenzene was removed via rotary evaporation, and then, the residual solid was washed with 20 mL of pentane. The solid was then collected and dried in a vacuum oven overnight at 80 °C to yield a dark-blue shimmery powder (crude yield = 74%). The material was purified via train sublimation prior to use.

**Bis(triphenyl Silyl Oxide) Silicon Phthalocyanine, (3PS)₂-SiPc.** To an oven-dried pressure vessel vessel were added (HO)₂-SiPc (0.3 g, 0.52 mmol) and nitrobenzene (17 mL). Argon gas was bubbled through the solution for 2 min. Triphenylsilane (1.35 g, 5.2 mmol) and tris(pentaphenylfluoroborate) (18.9 mg, 0.037 mmol) via the stock solution were added, and the vessel was submerged into an oil bath at 100 °C. A dose of 18.9 mg of tris(pentaphenylfluoroborate) (via the stock solution) and 1.35 g of triphenylsilane were added after 2.5, 5, and 7.5 h of reaction time. The reaction was monitored via silica TLC plates using a 1:1 hexanes/THF system. The reaction was then left for an additional 15 h before cooling to room temperature. Nitrobenzene was removed via rotary evaporation, and then, the residual solid was washed with 10 mL of pentane. The solid was then collected and dried in a vacuum oven overnight at 80 °C to yield a dark-aquamarine-blue powder (crude yield, incl. excess, unremoved triphenylsilane = 178%). The material was purified via train sublimation prior to use. LRMS (EI) m/z: [M] calcd for 1092.32; found, 1092.3. ¹HNMR (500 MHz, CDCl₃): δ 9.45 ppm (8 H, s), 8.29 (8 H, s), 6.68 (6 H, m), 6.28 (12 H, m), 4.78 (12 H, m).
temperature. The solution was filtered, and the filtrate was concentrated to dryness and then precipitated into methanol. The precipitate was filtered via vacuum filtration, washed with methanol and water, and dried at 50 °C under reduced pressure to yield a shiny blue powder (crude yield = 81%). The material was purified via train sublimation prior to use.

**Bis(tri-n-hexyl Silyl Oxide) Silicon Phthalocyanine, “BG” Method, BG-(3HS)-2SiPc.** BG-(3HS)-2SiPc was synthesized according to the literature. For example, a solution of 3.63 g (15.0 mmol) of tri-n-hexylchlorosilane, 0.94 g (23.5 mmol) of sodium hydroxide (crushed pellets), and 0.04 g of Aliquat HTA-I (Cognis) in 25 mL of chlorobenzene was stirred at room temperature. After 3 h, 2.87 g (4.7 mmol) of Cl2-SiPc was added, and the mixture was stirred and heated to 115 °C. After the second addition of tri-n-hexylchlorosilane, the reaction was left for an additional 4 h. The solution was cooled to room temperature and gravity-filtered. The filtrate was concentrated, and the residue was stirred with 10 mL of methanol, filtered with suction, washed with methanol and water, and dried at 50 °C under reduced pressure overnight to obtain a shiny blue powder (crude yield = 23%). The material was purified via train sublimation prior to use.

**Bis(tri-n-butyl Silyl Oxide) Silicon Phthalocyanine, “AQ” Method, AQ-(3BS)-2SiPc.** AQ-(3BS)-2SiPc was synthesized according to the literature. For example, a solution of 0.24 g (3.9 mmol) of tri-n-butylchlorosilane, 0.94 g (23.5 mmol) of sodium hydroxide (crushed pellets), and 0.04 g of Aliquat HTA-I (Cognis) in 25 mL of chlorobenzene was stirred at room temperature. After 3 h, 2.87 g (4.7 mmol) of Cl2-SiPc was added, and the mixture was stirred and heated to 115 °C. The precipitate was then collected and dried in a vacuum oven overnight at 80 °C to yield a dark-blue shimmery powder (crude yield = 102%). The material was purified via train sublimation prior to use. LRMS (EI) m/z [M] calcd, for 972.51; found, 972.5.

**Methods**

NMR spectra were recorded on an Agilent DD2 500 spectrometer at 23 °C in CDCl3, operating at 500 MHz for 1H NMR. Spin multiplicities are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Low-resolution mass spectrometry (LRMS) was performed on a GC Premier TOF mass spectrometer (Waters Corporation, Milford, Massachusetts, USA) with EI/CI sources or an AccuTOF model JMS-T1000LC mass spectrometer (JEOL USA Inc., Peabody, Massachusetts, USA) equipped with a Direct Analysis in Real Time (DART) ion source.

Electrochemistry was performed in a deoxygenated solvent (DCM) using a platinum wire counter electrode and a Ag/AgCl reference electrode. Tetrabutylammonium perchlorate (1 M) was used as the supporting electrolyte, and decamethylferrocene was used as an internal reference.

TGA (Q50 TA Instruments) was used to characterize the thermal properties under a blanket of nitrogen with a platinum boat. A heating rate of 5 °C min⁻¹ was used with the Ramp method until the desired temperature was reached. DSC was performed using a DSC Q1000 (TA Instruments) and was performed in the Heat Cool Heat mode, with a heating rate of 5 °C min⁻¹. The TGA/DSC traces, CV traces, UV–vis absorbance spectrum, NMR, and MS data are available in the Supporting Information.

**Associated Content**

TGA/DSC traces, CV traces, UV–vis absorbance spectrum, NMR, and MS data are available in the Supporting Information.

**Author Information**

**Corresponding Author**

Timothy P. Bender — Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada; Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario M5S 3E5, Canada; Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3H6, Canada; Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3E4, Canada; orcid.org/0000-0002-6086-7445; Email: tim.bender@utoronto.ca

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Notes
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