

## Synthesis and characterization of silicon phthalocyanines bearing axial phenoxy groups for attachment to semiconducting metal oxides

Jesse J. Bergkamp<sup>a</sup>, Benjamin D. Sherman<sup>a</sup>, Ernesto Mariño-Ochoa<sup>b</sup>, Rodrigo E. Palacios<sup>c</sup>, Gonzalo Cosa<sup>d</sup>, Thomas A. Moore<sup>\*a◇</sup>, Devens Gust<sup>\*a◇</sup> and Ana L. Moore<sup>\*a◇</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, Center for Bio-Inspired Solar Fuel Production, Arizona State University, Tempe, Arizona 85287-1604, USA

<sup>b</sup> Department of Chemistry, Tecnológico de Monterrey, Campus Monterrey, Monterrey, NL, 64849, México

<sup>c</sup> Departamento de Química, Facultad de Ciencias Exactas Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Río Cuarto, Córdoba 5800, Argentina

<sup>d</sup> Department of Chemistry, McGill University, Otto Maass Chemistry Building # 314, 801 Sherbrooke Street West, Montreal, QC, H3A 2K6, Canada

*Dedicated to Professor Karl M. Kadish on the occasion of his 65<sup>th</sup> birthday*

Received 1 May 2011

Accepted 14 June 2011

**ABSTRACT:** A series of axial phenoxy substituted octabutoxy silicon phthalocyanines bearing ethyl carboxylic ester and diethyl phosphonate groups have been prepared from the corresponding phenols in pyridine. Axial bis-hydroxy silicon phthalocyanine was prepared using an adaptation of a reported protocol [1, 2] from the octabutoxy free-base phthalocyanine. The phenols bear either carboxylic ester or phosphonate groups, which upon deprotection can serve as anchoring groups for attaching the phthalocyanines to semiconducting metal oxides used in dye sensitized solar cells (DSSCs). All the phthalocyanines of the series absorb in the near infra-red region: 758–776 nm. The first oxidation potential for each phenoxy derivative occurs near 0.55 V vs. SCE as measured by cyclic voltammetry, with all falling within a 10 mV range. This indicates that these dyes will have sufficient energy in the photo-excited state to drive the reduction of protons to hydrogen. Taking into account the absorption and electrochemical potentials, these dyes are promising candidates for use in dual-threshold photo-electrochemical cells.

**KEYWORDS:** silicon phthalocyanines, synthesis, electrochemistry, axial phenoxy linkage.

## INTRODUCTION

Developing artificial photosynthetic technologies for converting solar energy to transportable, energy-dense fuels would be a major step towards meeting future human

energy demands while also mitigating our impact on the environment [3]. Using the energy of sunlight to drive the conversion of water to oxygen and hydrogen offers an attractive means of converting and storing solar energy. A device capable of splitting water with light requires several key components, including catalysts for the oxidation of water and production of hydrogen and photo-chemical systems capable of generating and stabilizing charge separated states. The latter are of interest in this work and require light absorbing materials judiciously chosen for their absorbance and redox properties.

◇SPP full member in good standing

\*Correspondence to: Ana L. Moore, email: amoores@asu.edu, tel: +1 480-965-2953, fax: +1 480-965-2747; Devens Gust, email: gust@asu.edu and Thomas A. Moore, email: tom.moore@asu.edu

To date, artificial photosynthetic systems have suffered from high cost, a need for rare materials, and/or low overall efficiencies for generating hydrogen [4, 5]. An appealing route for incorporating potentially lower cost materials that enable fine-tuning of light absorption and the generation of long-lived, stable charged separated states lies in the use of organic dyes. Organic chromophores such as porphyrins, chlorins, perylenes, and phthalocyanines that bear carboxylic acid or phosphonate groups share many properties with natural dyes involved in photosynthesis and have demonstrated their viability in capturing and converting solar energy to electricity in dye sensitized solar cells as shown in recent reviews (Refs. 6 and 9) [6–9].

Producing an efficient device for the generation of hydrogen from water with the only energy input coming from light will likely require a design utilizing two light absorbing photosystems, each of which harvests distinct regions of the solar spectrum [10, 11]. When considering organic dyes for use in such a system, careful balance of the absorption and redox properties of the dyes plays an integral role in the design; in a dual-threshold cell, the dyes must interact with separate parts of the spectrum while still accessing similar solar flux, and the excited state energies and redox properties of each must provide sufficient driving force for its electrochemical reaction of interest.

Phthalocyanines are good candidates for use in dual-threshold photoelectrochemical cells because of their high extinction coefficients, good chemical stability, and, most importantly, excited state energies that provide sufficient driving force for the cathodic reduction of protons to hydrogen. Octabutoxy silicon phthalocyanines are of particular interest because of their absorbance in the visible and near-IR and the opportunity to functionalize them by covalent attachment to the axial position of the central silicon atom.

Herein we explore axially modifying silicon phthalocyanines to introduce desirable functional groups for integrating these dyes into photoelectrochemical cells. Axial substitution is an attractive feature for multiple synthetic reasons: (i) having substituents above and below the macrocycle prevents aggregation and increases the solubility of these compounds [12], (ii) the ligands can be highly functionalized, and (iii) silicon phthalocyanines are robust under harsh chemical treatments. Axially coordinated ruthenium phthalocyanines have been shown to photo-inject electrons into TiO<sub>2</sub> [13], demonstrating that the electronic coupling of axially-linked phthalocyanines is suitable for electron injection into semiconducting metal oxides. It is also worth noting that the use of non-peripheral octabutoxy groups helps to reduce aggregation [14], bathochromically-shifts the absorbance considerably relative to peripherally substituted analogs [15], and shifts the redox values to more negative potentials [16].

Here we report synthetic strategies for functionalizing far red absorbing octabutoxy silicon phthalocyanines for

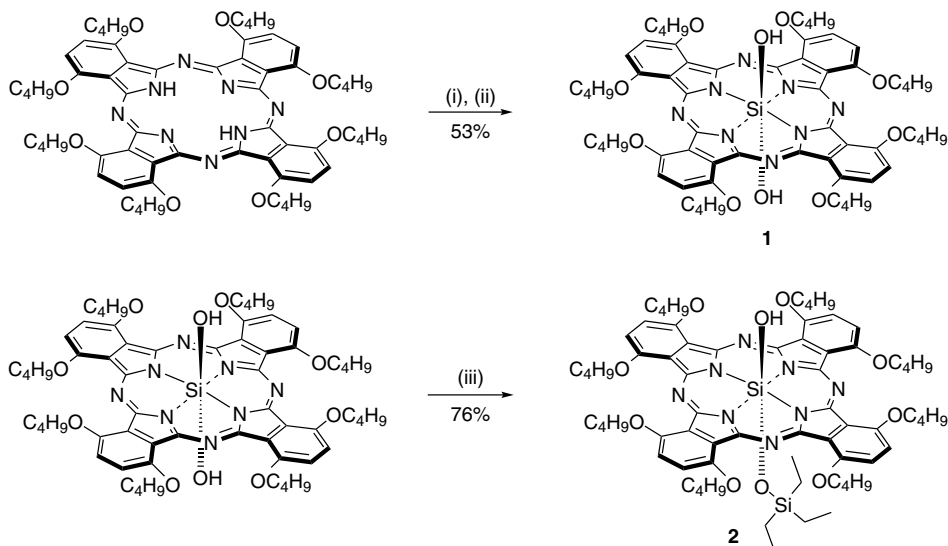
adsorption to metal oxide semiconductors. We have introduced phenyl or biphenyl axial substituents with ethyl carboxylic ester or diethyl phosphonate functional groups *via* a phenoxy linkage. Upon deprotection, the resulting carboxylate or phosphonate moieties would serve as anchoring groups to metal oxide semiconductors.

## RESULTS AND DISCUSSION

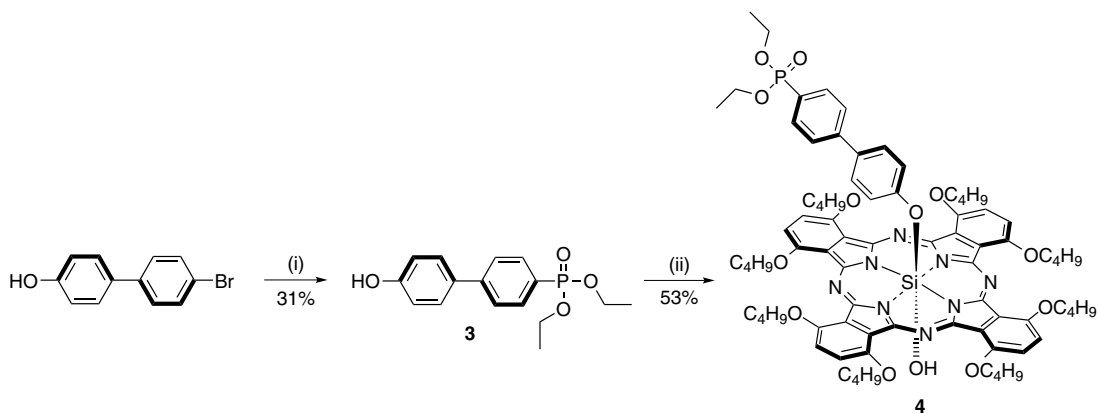
Joyner *et al.* [17] first reported a protocol for displacing axial hydroxy ligands on silicon phthalocyanines using molten phenol and a few drops of pyridine. Herein we report an adaptation of this method which yields monophenoxy silicon phthalocyanines. Silicon insertion into the free-base octabutoxy phthalocyanine involved first using trichlorosilane in a mixture of dichloromethane and tributylamine to yield the dichloride silicon phthalocyanine *in situ* (Scheme 1). Displacement of the chloride ligands in a mixture of water and triethylamine produced the dihydroxy silicon phthalocyanine **1** with a 53% yield (Scheme 1). Monosilation of **1** took place in refluxing toluene with one equivalent of chlorotriethylsilane to yield **2** with a 76% yield (Scheme 1). The reaction was monitored *via* thin layer chromatography and quenched upon formation of traces of the disilylated silicon phthalocyanine. Diethyl 4'-hydroxybiphenyl-4-ylphosphonate **3** was prepared by an adaptation of the Hirao palladium-catalyzed cross-coupling reaction [18] in dry dimethylformamide using tris(dibenzylideneacetone)-dipalladium(0) as the catalyst, diisopropylethylamine as the base, and 1,1'-bis(diphenylphosphino)ferrocene as the ligand (Scheme 2). The linkage of the corresponding phenols in compounds **4**, **5**, and **6** (Schemes 2 and 3) was done in pyridine at 55 °C for 48–60 h. In all cases, two column-chromatography steps were necessary for purification of **4**, **5**, and **6** due to the tendency for streaking on silica gel.

We started with a non-peripheral octaalkoxy substituted phthalocyanine for several reasons. Most importantly, alkoxy substituents aid in increasing the solubility of the phthalocyanine in organic solvents while inhibiting the tendency for aggregation [12, 14, 19]. Secondly, we have chosen octabutoxy groups located at the non-peripheral positions (1,4,8,11,15,18,22,25) because substitution at these sites has been shown to induce a greater shift on the absorption spectrum to longer wavelengths than octabutoxy groups on the peripheral positions [15].

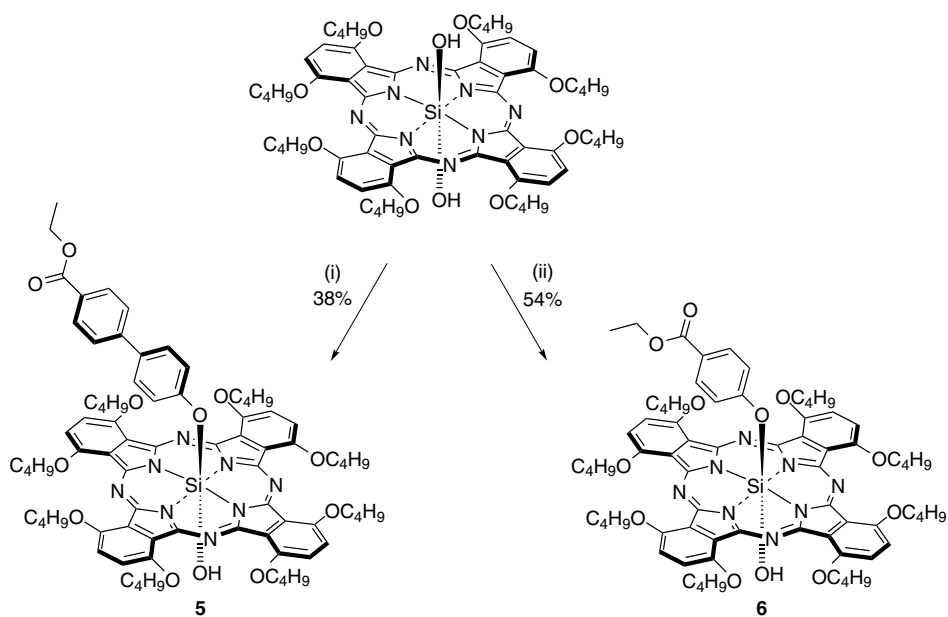
We have inserted silicon into the macrocycle of the phthalocyanine as this allows for axial covalent modification. Typically, axial modification of silicon phthalocyanines proceeds from the dichloride silicon phthalocyanine. However, we found the dichloride species to be unstable, possibly due to greater lability of the chloride ligands resulting from electron donating effects and increased solubility from the presence of the octabutoxy groups at the non-peripheral positions of the phthalocyanine macrocycle. Others have achieved the phenoxy linkage



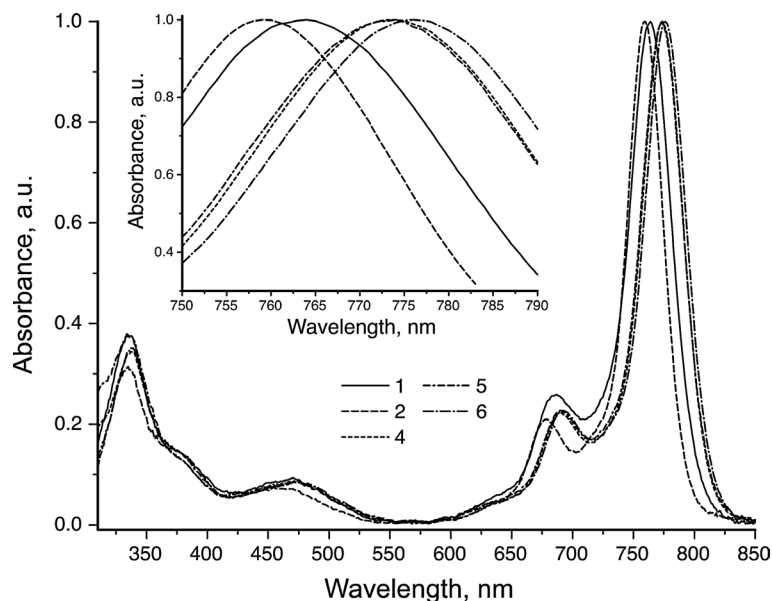
**Scheme 1.** Reaction conditions: (i)  $\text{HSiCl}_3$ , TBA,  $\text{CH}_2\text{Cl}_2$ , rt, 18 h; (ii) TEA,  $\text{H}_2\text{O}$ , rt, 3 h; (iii)  $\text{HSiEt}_3$ , toluene, pyridine, reflux, 45 min



**Scheme 2.** Reaction conditions: (i) dimethylformamide, diethylphosphite, diisopropylethylamine (Hünig's base), 1,1'-bis(diphenylphosphino)ferrocene, tris(dibenzylideneacetone)dipalladium(0), 110 °C, 24 h; (ii) **1**, pyridine, 55 °C, 48 h



**Scheme 3.** Reaction conditions: (i) ethyl 4'-hydroxybiphenyl-4-carboxylate, pyridine, 55 °C, 48 h; (ii) ethyl 4-hydroxybenzoate, pyridine, 55 °C, 60 h



**Fig. 1.** Normalized absorption spectra for phthalocyanine derivatives **1**, **2**, **4**, **5**, and **6**. Inset shows an expanded view of the longest wavelength Q-band of each derivative. Spectra were taken in distilled dichloromethane

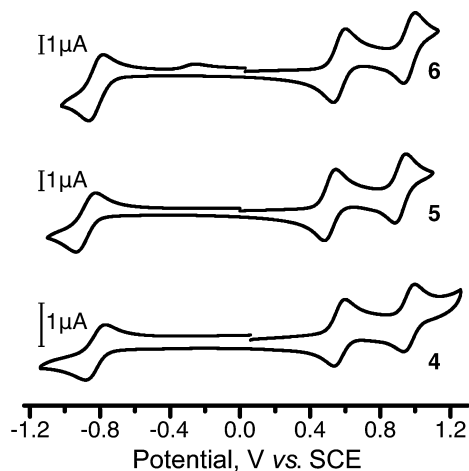
[12, 16, 20, 21], but started from the non-substituted dichloride silicon phthalocyanine and allowed it to react with a strong base such as sodium hydride. Our method starts from the dihydroxy species, as demonstrated by Joyner and others [17, 22], but requires only mild reaction conditions (such as lower temperatures), limited amounts of starting phenol, and allows use of phenols with chemically sensitive functional groups. Furthermore, it allows for the synthetic control necessary to produce the mono axial phenoxy substituted silicon phthalocyanine.

Initially we set out to synthesize mono-phenoxy phthalocyanine with the opposite face protected with a triethylsilyl group. This strategy resulted in two issues of concern: (i) the longest wavelength Q-band was blue shifted in **2** with respect to **1** by 5 nm (Fig. 1), and, (ii) after the phenoxy group is coupled, the stability of the triethylsilyl group decreases as evidenced by difficulties in isolation. Therefore we decided to leave the second axial hydroxyl group unprotected.

Ultraviolet-visible spectral analysis reveals a shift to longer wavelengths of the last Q-band upon phenoxy displacement of the hydroxide. Compound **6** shows a bathochromic shift of 12 nm with respect to **1** (Fig. 1) with the last Q-band occurring at 776 nm. Both **4** and **5** have the biphenyl linker and, although they bear different functional groups at the *para* position, their absorption properties are similar in that the last Q-band is slightly shifted to shorter wavelengths in comparison with **6** but longer wavelengths with respect to **1** (Fig. 1). The absorbance of the last Q-bands of **4** and **5** indicates that the ethyl carboxylic ester or diethyl phosphonate groups do not have as strong an influence on the absorbance presumably due to decoupling caused by the biphenyl linker.

The  $^1\text{H}$  NMR spectra of **4**, **5**, and **6** show an upfield shift of the aromatic protons that are axial to the plane of the phthalocyanine. Aromatic protons *ortho* to the phenoxy linkage show signals at  $\sim 2.9$  ppm, consistent with results from other studies [23]. The magnitude of the up field shift decreases as the location of the proton moves further away from the center of the phthalocyanine macrocycle which is in accordance with the literature [24–27]. The OH signal in the  $^1\text{H}$  NMR of **2**, **4**, **5**, and **6** could not be detected; Cook *et al.* have observed similar effects [28]. Each target compound was characterized by matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectroscopy. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldene]-malononitrile was found to be the best matrix and free-base 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine was used as an internal reference.

An important aspect of evaluating dyes for photoelectrochemical applications lies in the determination of their redox properties in order to ensure that they can carry out the photo-initiated electrochemical processes of interest. We are targeting silicon phthalocyanines in this work to drive the cathodic reduction of protons to hydrogen; their excited state redox potentials must be sufficiently negative to carry out this process, which at pH 7 occurs at  $-0.65$  V vs. SCE. Determining the potentials for the oxidation and reduction of a dye, coupled with its absorption characteristics, allows approximation of its excited state redox potentials. Cyclic voltammetry experiments on the silicon phthalocyanine



**Fig. 2.** Cyclic voltammograms for compounds **4**, **5**, and **6**. All scans shown were taken at 100 mV/s in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate. The identity of the phenoxy ligand had only subtle influence on the redox potentials as evidenced by the similarity of each scan



**Table 1.** Redox values for the compounds **1**, **4**, **5**, and **6**. Potentials given are in reference to a standard calomel electrode (SCE). Peak separation ( $\Delta E_p$ ) of the anodic and cathodic scans is given for each process

Compound	Ox(1), ( $\Delta E_p$ )	Ox(2), ( $\Delta E_p$ )	Red(1), ( $\Delta E_p$ )
<b>1</b>	0.55 V, (64 mV)	0.95 V, (67 mV)	-0.84 V, (80 mV)
<b>4</b>	0.55 V, (63 mV)	0.96 V, (64 mV)	-0.90 V, (98 mV)
<b>5</b>	0.54 V, (64 mV)	0.96 V, (64 mV)	-0.83 V, (98 mV)
<b>6</b>	0.54 V, (68 mV)	0.93 V, (67 mV)	-0.82 V, (80 mV)

dyes synthesized for this work showed them to be good candidates for driving proton reduction. Figure 2 features cyclic voltammograms for compounds **4**, **5**, and **6**; the redox potentials for these compounds and dye **1** are listed in Table 1. Overall, the identity of the axial ligand to the silicon had minimal influence on the redox potentials of the phthalocyanines. For example, the potentials for the first oxidation differed by only 10 mV across the series. These molecules showed reversible first and second oxidations with anodic and cathodic peak separations ( $\Delta E_p$ ) near 60 mV, while the first reductions gave greater peak separations, implying more quasi-reversible character.

With an eye toward the eventual testing of these dyes in a dual-threshold photoelectrochemical water splitting cell, we are most interested in the potential of the first oxidation. With midpoint potentials near 0.55 V vs. SCE and longest-wavelength photon absorption of  $\sim 1.6$  eV, these dyes will have adequate excited state energies to sensitize  $\text{TiO}_2$  or other semiconducting metal oxides with a more negative conduction band [29]. Future work will aim at investigating the efficiency of electron injection into metal oxide semiconductors by these axial functionalized phthalocyanines, and their ability to drive the formation of hydrogen in a photoelectrochemical cell.

## EXPERIMENTAL

### Electrochemistry

All electrochemical experiments were carried out with a CH Instruments 760D potentiostat. All samples were analyzed in a closed glass cell under an argon atmosphere with a three electrode setup. A working platinum disc electrode was used in concert with a platinum mesh counter electrode and a silver quasi-reference electrode. The potential of the silver quasi-reference electrode was calibrated vs. the ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple at the conclusion of each series of experiments with the  $\text{Fc}^+/\text{Fc}$  couple taken as 0.45 V vs. SCE. Distilled dichloromethane was used as the working solvent along with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, which was doubly recrystallized from ethanol and dried under reduced pressure with heat prior to use.

### Materials

Dichloromethane used for synthesis and electrochemistry was refluxed over calcium hydride followed by distillation and storage over activated 4 Å molecular sieves. Pyridine and dimethylformamide were dried over activated 4 Å molecular sieves. Tributylamine was passed through activated alumina and stored overnight over activated 4 Å molecular sieves. Toluene for synthesis was distilled from phosphorus pentoxide and stored over activated 4 Å molecular sieves. Toluene, ethyl acetate and hexane used for column chromatography were distilled. Triethylamine was purchased from Alfa Aesar and used without further purification. Trichlorosilane, 1,4,8,11,15,18,22,25-octabutoxy-29*H*,31*H*-phthalocyanine, chlorotriethylsilane, diethylphosphite, diisopropylethylamine (Hünig's base), 1,1'-bis(diphenylphosphino)ferrocene, 4'-bromo-(1,1'-biphenyl)-4-ol, ethyl 4'-hydroxybiphenyl-4-carboxylate, ethyl 4-hydroxybenzoate, and tris(dibenzylideneacetone)-dipalladium(0) were purchased from Sigma-Aldrich and used without further purification. Tetrabutylammonium hexafluorophosphate was also purchased from Sigma-Aldrich. Thin layer chromatography plates (250 micron), both fluorescent and non-fluorescent, were purchased from Analtech, Inc. Silica gel (SilicaFlash F60 40–63  $\mu\text{m}$ ) used for column chromatography was purchased from SILICYCLE.

### General

$^1\text{H}$  NMR spectra were recorded on a 400 MHz Varian Liquid-State spectrometer. NMR samples were dissolved in deuteriochloroform with 0.03% tetramethylsilane as an internal reference. Mass spectra were obtained on an Applied Biosystems Voyager-DE STR matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). The matrix used for all mass spectra samples was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile. Ultraviolet-visible ground state absorption spectra were measured using a Shimadzu UV2100U spectrophotometer. All ultraviolet-visible samples were dissolved in distilled dichloromethane.

### Synthesis

**Dihydroxy-1,4,8,11,15,18,22,25-octabutoxyphthalocyaninato-silicon(IV) (1).** A portion of 1,4,8,11,15,18,22,25-octabutoxy-29*H*,31*H*-phthalocyanine (1.1 g, 1.0 mmol) was dissolved in dry dichloromethane (240 mL) and dry tributylamine (24 mL). The solution was degassed with argon for 10 min, followed by addition of trichlorosilane (2.4 mL, 23.8 mmol) and allowed to stir at room temperature for 18 h under argon. Triethylamine (80 mL) was added carefully, followed by  $\text{H}_2\text{O}$  (40 mL) and the mixture was allowed to stir at room temperature for an additional 3 h. To neutralize the amines, aqueous HCl

(12 M, 58 mL) was added until the solution was acidic, and the solution was allowed to stir for an additional 1 h. The mixture was filtered and the solid was washed with dichloromethane (500 mL). The mother liquor was separated and the organic layer was washed twice with HCl (1 M, 100 mL) followed by 3 washes with H<sub>2</sub>O. The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. Column chromatography was done using silica gel with ethyl acetate/toluene (50:50) as eluent, which afforded a green solid. Yield 615 mg (53%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; 0.03% Me<sub>4</sub>Si): δ<sub>H</sub>, ppm -2.54 (2H, bs, -OH), 1.08 (24H, t, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 1.66 (16H, sex., -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 2.20 (16H, p, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 4.87 (16H, t, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 7.64 (8H, s, PcH). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>, nm 334, 470, 687, 764. MS (MALDI-TOF): *m/z* calcd. for C<sub>64</sub>H<sub>82</sub>N<sub>8</sub>O<sub>10</sub>Si 1150.59, obsd. 1150.59.

**Triethylsilylhydroxy-1,4,8,11,15,18,22,25-octabutoxyphthalocyaninatosilicon(IV) (2).** A portion of (1) (70 mg, 0.06 mmol) was dissolved in dry toluene (30 mL) and dry pyridine (4 mL) and degassed for 15 min. Chlorotriethylsilane (10.2 μL, 0.06 mmol) was added and the solution was allowed to reflux for 45 min. Once formation of bis-triethylsilyl phthalocyanine was observed (monitored by TLC), the solvent was removed under reduced pressure and column chromatography was done using silica gel with toluene/ethyl acetate (65:35) as eluent, which afforded a green solid. Yield 59 mg (76%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; 0.03% Me<sub>4</sub>Si): δ<sub>H</sub>, ppm -2.14 (6H, q, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 8 Hz), -0.98 (9H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 8 Hz), 1.04 (24H, t, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 1.63 (16H, sex., -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 2.15 (16H, p, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 4.88 (16H, m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 7.65 (8H, s, PcH). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>, nm 335, 465, 679, 759. MS (MALDI-TOF): *m/z* calcd. for C<sub>70</sub>H<sub>96</sub>N<sub>8</sub>O<sub>10</sub>Si<sub>2</sub> 1264.68, obsd. 1264.68.

**Diethyl (4'-hydroxy-[1,1'-biphenyl]-4-yl)phosphonate (3).** A portion of 4'-bromo-(1,1'-biphenyl)-4-ol (996 mg, 4.0 mmol) was dissolved in dimethylformamide (15 mL) and the solution was degassed with argon for 15 min. To that solution was added diethylphosphite (662 mg, 4.8 mmol), diisopropylethylamine (Hünig's base) (0.9 mL), 1,1'-bis(diphenylphosphino)ferrocene (24.3 mg, 0.044 mmol) and tris(dibenzylideneacetone)-dipalladium(0) (26.9 mg, 0.040 mmol, 1 mol.%). The solution was allowed to stir at 110 °C for 24 h under argon. The solvent was removed under reduced pressure and the red-yellow oil dissolved in ethyl acetate, H<sub>2</sub>O was added (50 mL) and the aqueous layer was washed four times with ethyl acetate followed by one wash with brine, dried over magnesium sulfate and concentrated. Column chromatography was done using silica gel with ethyl acetate/hexane (70:30) as eluent, which afforded a yellow solid. Yield 378 mg (31%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; 0.03% Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 1.35 (6H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 4.15 (4H, m, -CH<sub>2</sub>-CH<sub>3</sub>), 6.87 (2H, d, Ar-phenoxy,

*J* = 8.8 Hz), 7.47 (2H, d, Ar-phenoxy, *J* = 8.8 Hz), 7.63 (2H, m, Ar-phosphonate), 7.84 (2H, m, Ar-phosphonate). MS (MALDI-TOF): *m/z* calcd. for C<sub>16</sub>H<sub>19</sub>O<sub>4</sub>P 306.10, obsd. 307.11.

**4'-(Diethoxyphosphoryl)biphenyl-4-olatehydroxy-1,4,8,11,15,18,22,25-octabutoxyphthalocyaninatosilicon(IV) (4).** A portion of (1) (31 mg, 0.027 mmol) was dissolved in dry pyridine (10 mL), to this solution was added diethyl 4'-hydroxybiphenyl-4-ylphosphonate (3) (82 mg, 0.27 mmol) and the solution was degassed with argon for 10 min. The solution was allowed to stir at 55 °C for 48 h under argon. The solvent was removed under reduced pressure and two column chromatography steps were needed to purify the desired product using silica gel. The first chromatography step was with toluene/ethyl acetate (60:40) and the second with toluene/ethyl acetate (75:25) to afford a green solid. Yield 20 mg (53%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; 0.03% Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 1.04, (24H, t, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 1.22 (6H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 6.8 Hz), 1.62 (16H, sex., -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 2.14 (16H, p, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 8 Hz), 2.94 (2H, d, Ar-phenoxy, *J* = 8.8 Hz), 3.98 (4H, m, -CH<sub>2</sub>-CH<sub>3</sub>), 4.82 (16H, m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 5.96 (2H, d, Ar-phenoxy, *J* = 8.8 Hz), 6.87 (2H, m, Ar-phosphonate), 7.49 (2H, m, Ar-phosphonate) 7.65 (8H, s, PcH). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>, nm 339, 472, 691, 774. MS (MALDI-TOF): *m/z* calcd. for C<sub>80</sub>H<sub>99</sub>N<sub>8</sub>O<sub>13</sub>PSi 1438.68, obsd. 1438.69 and 1133.59 (M-phenoxy).

**4'-(Ethoxycarbonyl)biphenyl-4-olatehydroxy-1,4,8,11,15,18,22,25-octabutoxyphthalocyaninatosilicon(IV) (5).** A portion of (1) (48 mg, 0.042 mmol) was dissolved in dry pyridine (10 mL) and the solution degassed for 10 min. To this solution was added ethyl 4'-hydroxybiphenyl-4-carboxylate (51 mg, 0.21 mmol) and allowed to stir at 55 °C for 48 h under argon. The solvent was removed under reduced pressure and column chromatography was done using silica gel with toluene/ethyl acetate (65:35) and then a second column chromatography step using toluene/ethyl acetate (75:25) as eluent, afforded a green solid. Yield 22 mg (38%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; 0.03% Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 1.04, (24H, t, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 1.31 (3H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 1.62 (16H, sex., -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.6 Hz), 2.14 (16H, p, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 8 Hz), 2.93 (2H, d, Ar-phenoxy, *J* = 8.8 Hz), 4.27 (2H, q, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 4.81 (16H, m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 5.98 (2H, d, Ar-phenoxy, *J* = 8.4 Hz), 6.83 (2H, d, Ar-benzoate, *J* = 8.8 Hz), 7.64 (8H, s, PcH), 7.72 (2H, d, Ar-benzoate, *J* = 8.4 Hz). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>, nm 338, 471, 690, 774. MS (MALDI-TOF): *m/z* calcd. for C<sub>79</sub>H<sub>94</sub>N<sub>8</sub>O<sub>12</sub>Si 1374.68, obsd. 1374.68.

**4-(Ethoxycarbonyl)phenolatehydroxy-1,4,8,11,15,18,22,25-octabutoxyphthalocyaninatosilicon(IV) (6).** A portion of (1) (48 mg, 0.042 mmol) was dissolved in dry pyridine (12 mL) and the solution degassed for 10 min. To this solution was added ethyl 4-hydroxybenzoate (35 mg, 0.21 mmol) and was allowed to stir at

55 °C for 60 h under argon. The solvent was removed under reduced pressure and column chromatography was done using silica gel with toluene/ethyl acetate (70:30) as solvent. A second column chromatography step using toluene/ethyl acetate (80:20) as eluent, afforded a green solid. Yield 29 mg (54%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; 0.03% Me<sub>4</sub>Si): δ<sub>H</sub>, ppm 1.07, (24H, t, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 1.34 (3H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 1.64 (16H, sex., -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.2 Hz), 2.16 (16H, p, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, *J* = 8 Hz), 2.87 (2H, d, Ar-phenoxy, *J* = 8.8 Hz), 3.91 (2H, q, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 6.8 Hz), 4.80 (16H, m, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 6.41 (2H, d, Ar-phenoxy, *J* = 8.8 Hz), 7.65 (8H, s, PcH). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>, nm 337, 471, 692, 776. MS (MALDI-TOF): *m/z* calcd. for C<sub>73</sub>H<sub>90</sub>N<sub>8</sub>O<sub>12</sub>Si 1298.64, obsd. 1298.65 and 1133.58 (M-phenoxy).

## CONCLUSION

The synthesis of silicon octabutoxy phthalocyanines bearing axial ethyl carboxylic esters and diethylphosphonate groups *via* a phenoxy linkage can be accomplished in a few synthetic steps, from a variety of phenols, and under mild conditions. Additionally, this approach allows for isolation of the mono axial functionalized phenoxy phthalocyanines. Strongly red absorbing phthalocyanines are good candidates for dual-threshold solar cells and the use of non-peripheral octabutoxy groups as well as the substitution of phenols on the axial position of silicon phthalocyanines, as demonstrated with **4**, **5**, and **6**, helps to further shift their absorption to the near infrared. Furthermore, the phenoxy substituted phthalocyanines prepared in this study demonstrated potentials for the first oxidation near 0.55 V *vs.* SCE, making them good candidates for photosensitizing low-potential conduction band metal oxide semiconductors. The ability to use low-potential conduction band materials will provide more driving force for the generation of hydrogen from water. By incorporating phenoxy ligands with functional groups that can anchor to metal oxide semiconductors, we are progressing toward the use of these dyes in dual-threshold photoelectrochemical cells designed to carry out overall water splitting with sunlight. Moreover the ability to bind a variety of phenoxy derivatives in the axial position can be exploited to control the macrocycle to metal-oxide electronic coupling and consequently the efficiency of the sensitization process. The synthetic strategy presented offers a route to obtaining phthalocyanines with axial groups for anchoring to semiconducting metal oxides from the readily obtainable bis-hydroxy octabutoxy silicon phthalocyanines.

## Acknowledgements

This work was supported in part by a grant from the National Science Foundation, USA (DMR-0908656), the Agencia Nacional de Promoción Científica y Tecnológica,

Argentina (PRH 23 PICT 140/08), the Consejo Nacional de Ciencia y Tecnología, México (101939), the National Science and Engineering Research Council (Canada) and a Tomlinson Award, McGill University. The research of J.J.B, B.D.S, T.A.M, D.G. and A.M. was supported as part of the Center for Bio-Inspired Solar Fuel Production, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001016. R.E.P. is a permanent research staff of CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina). We would also like to acknowledge John Lopez and Zach Laughrey from the ASU Proteomics and Protein Chemistry Facility for obtaining MALDI-TOF mass spectra. B.D.S thanks Science Foundation Arizona for their support of this work through a graduate research fellowship.

## REFERENCES

- Ranta J, Viljanen R, Lemmetyinen H and Efimov A. *Dyes Pigm.* 2009; **83**: 317–323.
- Aoudia M, Cheng GZ, Kennedy VO, Kenney ME and Rodgers MAJ. *J. Am. Chem. Soc.* 1997; **119**: 6029–6039.
- Hambourger M, Moore GF, Kramer DM, Gust D, Moore AL and Moore TA. *Chem. Soc. Rev.* 2009; **38**: 25–35.
- Khaselev O and Turner JA. *Science* 1998; **280**: 425–427.
- Youngblood WJ, Lee SHA, Kobayashi Y, Hernandez-Pagan EA, Hoertz PG, Moore TA, Moore AL, Gust D and Mallouk TE. *J. Am. Chem. Soc.* 2009; **131**: 926–927.
- Walter MG, Rudine AB and Wamser CC. *J. Porphyrins Phthalocyanines* 2010; **14**: 759–792.
- Muthukumar K, Loewe RS, Ambroise A, Tamaru SI, Li QL, Mathur G, Bocian DF, Misra V and Lindsey JS. *J. Org. Chem.* 2004; **69**: 1444–1452.
- Loewe RS, Ambroise A, Muthukumar K, Padmaja K, Lysenko AB, Mathur G, Li QL, Bocian DF, Misra V and Lindsey JS. *J. Org. Chem.* 2004; **69**: 1453–1460.
- Martinez-Diaz MV, de la Torrea G and Torres T. *Chem. Commun.* 2010; **46**: 7090–7108.
- Hanna MC and Nozik AJ. *J. Appl. Phys.* 2006; **100**.
- Blankenship RE, Tiede DM, Barber J, Brudvig GW, Fleming G, Ghirardi M, Gunner MR, Junge W, Kramer DM, Melis A, Moore TA, Moser CC, Nocera DG, Nozik AJ, Ort DR, Parson WW, Prince RC and Sayre RT. *Science* 2011; **332**: 805–809.
- Cosut B, Yesilot S, Durmus M, Kilic A and Ahsen V. *Polyhedron.* 2010; **29**: 675–682.
- O'Regan BC, Lopez-Duarte I, Martinez-Diaz MV, Forneli A, Albero J, Morandeira A, Palomares E, Torres T and Durrant JR. *J. Am. Chem. Soc.* 2008; **130**: 2906–2907.

14. Cook MJ, Dunn AJ, Daniel MF, Hart RCO, Richardson RM and Roser SJ. *Thin Solid Films* 1988; **159**: 395–404.
15. Ke MR, Huang JD and Weng SM. *J. Photochem. Photobiol. A* 2009; **201**: 23–31.
16. Ermilov EA, Tannert S, Werncke T, Choi MTM, Ng DKP and Roder B. *Chem. Phys.* 2006; **328**: 428–437.
17. Joyner RD, Cekada J, Linck RG and Kenney ME. *J. Inorg. Nucl. Chem.* 1960; **15**: 387–388.
18. Belabassi Y, Alzghari S and Montchamp JL. *J. Organomet. Chem.* 2008; **693**: 3171–3178.
19. Li ZY and Lieberman M. *Inorg. Chem.* 2001; **40**: 932–939.
20. Huang JD, Jiang XJ, Shen XM and Tang QQ. *J. Porphyrins Phthalocyanines* 2009; **13**: 1227–1232.
21. Maree MD, Nyokong T, Suhling K and Phillips D. *J. Porphyrins Phthalocyanines* 2002; **6**: 373–376.
22. Maree MD and Nyokong T. *J. Porphyrins Phthalocyanines* 2001; **5**: 555–563.
23. Leng XB and Ng DKP. *Eur. J. Inorg. Chem.* 2007; 4615–4620.
24. Koyama T, Suzuki T, Hanabusa K, Shirai H and Kobayashi N. *Inorg. Chim. Acta* 1994; **218**: 41–45.
25. Janson TR, Kane AR, Sullivan JF, Knox K and Kenney ME. *J. Am. Chem. Soc.* 1969; **91**: 5210.
26. Davison JB and Wynne KJ. *Macromolecules* 1978; **11**: 186–191.
27. Palacios RE, Kodis G, Herrero C, Ochoa EM, Gervaldo M, Gould SL, Kennis JTM, Gust D, Moore TA and Moore AL. *J. Phys. Chem. B.* 2006; **110**: 25411–25420.
28. Zhao ZX, Cammidge AN, Hughes DL and Cook MJ. *Org. Lett.* 2010; **12**: 5138–5141.
29. Durr M, Rosselli S, Yasuda A and Nelles G. *J. Phys. Chem. B* 2006; **110**: 21899–21902.