

Dye sensitization of polymer/fullerene solar cells incorporating bulky phthalocyanines

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ABSTRACT

The light-harvesting efficiency of P3HT:PCBM solar cells can be improved by incorporating near-IR dye molecules such as silicon phthalocyanine derivatives with bulky axial groups (SiPc). In order to study the size effect of the axial groups on the dye sensitization in P3HT:PCBM solar cells, we synthesized five SiPc derivatives with different axial groups: SiPc[OSi(C_nH_{2n+1})₃]₂ (SiPcn, *n* = 2, 3, 4, 6) and SiPc[OSi(iBu)₂C₁₈H₃₇]₂ (SiPcB18). The power conversion efficiency (PCE) increased in the order of *n* = 2–4, reached the maximum at around *n* = 4 and 6, and then decreased for SiPcB18 with the longest axial groups. As a result, the PCE was improved to 4.2%, which is larger by 10% than that of P3HT:PCBM control cells without dye molecules. We therefore conclude that the butyl or hexyl chain in the axial ligand is the most appropriate for the dye sensitization in P3HT:PCBM solar cells.

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1. Introduction

Polymer solar cells based on a blend of a conjugated polymer and a fullerene derivative have attracted interest because of their potential to be lightweight, flexible, solution processable, and hence cost-effective [1–5]. Among them, the blend of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) has been most widely studied as the active layer in polymer/fullerene solar cells. This polymer solar cell exhibits high external quantum efficiency (EQE) and fill factor (FF) [6–10], which are still the highest in polymer solar cells. However, P3HT can harvest only up to ~650 nm, which corresponds to only a quarter of the total photons in the solar light. In order to harvest a broader range of the solar light, various low-bandgap polymers have been developed in recent years [11–14]. On the other hand, dye sensitization based on a ternary blend of polymer/fullerene/dye has been recently reported as another approach to expand the light-harvesting range by several groups including ours [15–19].

We have shown that the light-harvesting efficiency of P3HT:PCBM solar cells can be improved by incorporating silicon phthalocyanine bis(trihexylsilyl oxide) (SiPc6) [16]. Furthermore, we demonstrated that the light-harvesting bandwidth can be

expanded by multi-colored sensitization with SiPc6 and silicon naphthalocyanine bis(trihexylsilyl oxide) (SiNc6), which have complementary absorption bands in the near-IR region [17]. The bulky trihexylsilyl oxide group can effectively suppress dye aggregation even in solid films and therefore is considered to be one of the keys to success. However, such bulky substituents could hinder the charge transfer between the neighboring molecules. In other words, little is known about the appropriate size of substituents for dye-sensitized polymer/fullerene solar cells.

In this study, we synthesized a series of SiPc derivatives with the same two trialkylsilyl oxide axial groups –OSi(C_nH_{2n+1})₃ to study the size effect of bulky axial groups on the dye sensitization in polymer/fullerene solar cells. The alkyl chains of the two axial groups systematically vary from ethyl to hexyl in SiPc[OSi(C_nH_{2n+1})₃]₂ (SiPcn, *n* = 2, 3, 4, 6) and the longest of octadecyl in SiPc[OSi(iBu)₂C₁₈H₃₇]₂ (SiPcB18). Herein we discuss the device performance of P3HT:PCBM:dye ternary blend solar cells in terms of steric structures of dye molecules.

2. Experimental

2.1. Synthesis of dye derivatives

Fig. 1 shows the reaction schemes and the chemical structures of SiPc derivatives with various axial groups employed in this study. The axial substituents are summarized in Table 1. Details of the synthesis are described below.

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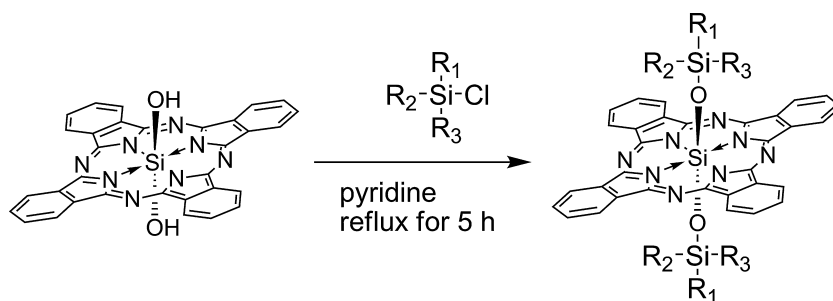


Fig. 1. Synthetic schemes of SiPc[OSi(C_nH_{2n+1})₃]₂ (SiPc_n, n = 2, 3, 4, 6) and SiPc[OSi(iBu)₂C₁₈H₃₇]₂ (SiPcB18).

SiPc[OSi(C₂H₅)₃]₂ (SiPc2): A mixture of SiPc(OH)₂ (72.4 mg), chlorotriethylsilane (200 μL), and dry pyridine (10 mL) was refluxed for 5 h. After the solution obtained cooled, the solvent was evaporated and chloroform was added to the residue. The solution was washed with saturated NaCl solution, and then dried over MgSO₄. After evaporation of the solvent, the residue was purified by silica gel column chromatography (toluene/hexane = 3/1 (v/v) as eluent) to afford SiPc2 (21.4 mg) as a blue solid (yield = 21%).

TLC (toluene/hexane = 3/1 (v/v)): R_f = 0.85

¹H NMR (400 MHz, CDCl₃): δ = 9.65 (m, 3,6-Pc, 8H), 8.33 (m, 4,5-Pc, 8H), -1.24 (t, CH₃, 18H), -2.44 (m, α-CH₂, 12H)

UV/Vis (CHCl₃): λ_{max} = 669 nm (ε = 2.6 × 10⁵ M⁻¹ cm⁻¹)

SiPc[OSi(C₃H₇)₃]₂ (SiPc3): A mixture of SiPc(OH)₂ (75.0 mg), chlorotripropylsilane (180 μL), and dry pyridine (10 mL) was refluxed for 5 h. After the solution obtained cooled, the solvent was evaporated and the residue was washed with pentane. After evaporation of the solvent, the residue was purified by silica gel column chromatography (toluene/hexane = 2/1 (v/v) as eluent) to afford SiPc3 (44.0 mg) as a blue solid (yield = 38%).

TLC (toluene/hexane = 2/1 (v/v)): R_f = 0.92

¹H NMR (400 MHz, CDCl₃): δ = 9.65 (m, 3,6-Pc, 8H), 8.34 (m, 4,5-Pc, 8H), -0.31 (t, CH₃, 18H), -1.17 (m, β-CH₂, 12H), -2.43 (m, α-CH₂, 12H)

UV/Vis (CHCl₃): λ_{max} = 668 nm (ε = 3.0 × 10⁵ M⁻¹ cm⁻¹)

SiPc[OSi(C₄H₉)₃]₂ (SiPc4): A mixture of SiPc(OH)₂ (75.4 mg), chlorotributylsilane (210 μL), and dry pyridine (10 mL) was refluxed for 5 h. After the solution obtained cooled, the solvent was evaporated and the residue was washed with pentane. After evaporation of the solvent, the residue was purified by silica gel column chromatography (toluene/hexane = 1/1 (v/v) as eluent) to afford SiPc4 (81.2 mg) as a blue solid (yield = 70%).

TLC (toluene/hexane = 1/1 (v/v)): R_f = 0.90

¹H NMR (400 MHz, CDCl₃): δ = 9.64 (m, 3,6-Pc, 8H), 8.33 (m, 4,5-Pc, 8H), 0.05 (m, γ-CH₂, CH₃, 30H), -1.26 (m, β-CH₂, 12H), -2.43 (m, α-CH₂, 12H)

UV/Vis (CHCl₃): λ_{max} = 668 nm (ε = 2.9 × 10⁵ M⁻¹ cm⁻¹)

SiPc[OSi(C₆H₁₃)₃]₂ (SiPc6): A mixture of SiPc(OH)₂ (74.7 mg), chlorotrihexylsilane (500 μL), and dry pyridine (10 mL) was refluxed for 5 h. After the solution obtained cooled, the solvent was evaporated and the residue was added chloroform. The solution was washed with saturated NaCl solution, and then dried over MgSO₄. After evaporation of the solvent, the residue was purified by silica gel column chromatography (toluene/hexane = 1/2 (v/v) as eluent) to afford SiPc6 (38 mg) as a blue solid (yield = 25%).

TLC (toluene/hexane = 1/2 (v/v)): R_f = 0.87

¹H NMR (400 MHz, CDCl₃): δ = 9.63 (m, 3,6-Pc, 8H), 8.31 (m, 4,5-Pc, 8H), 0.81 (m, ε-CH₂, 12H), 0.71 (t, CH₃, 18H), 0.36 (m, δ-CH₂, 12H), 0.02 (m, γ-CH₂, 12H), -1.28 (m, β-CH₂, 12H), -2.45 (m, α-CH₂, 12H)

UV/Vis (CHCl₃): λ_{max} = 668 nm (ε = 3.0 × 10⁵ M⁻¹ cm⁻¹)

SiPc[OSi(iBu)₂C₁₈H₃₇]₂ (SiPcB18): A mixture of SiPc(OH)₂ (99.5 mg), chlorodiisobutyloctadecylsilane (520 μL), and dry pyridine (25 mL) was refluxed for 5 h. After the solution obtained cooled, the solvent was evaporated and the residue was washed with water, and then dried over MgSO₄. After evaporation of the solvent, the residue was purified by silica gel column chromatography (toluene/hexane = 1/3 (v/v) as eluent) to afford SiPcB18 (150 mg) as a blue solid (yield = 64%).

TLC (toluene/hexane = 1/3 (v/v)): R_f = 0.90

¹H NMR (400 MHz, CDCl₃): δ = 9.62–9.64 (m, α-Pc, 8H), 8.30–8.32 (m, β-Pc, 8H), 1.33–0.84 (m, CH₂, 58H), 0.42 (m, δ-C₁₈H₃₅, 4H), 0.08 (m, γ-C₁₈H₃₅, 4H), -0.55 (m, γ-iBu, 24H), -0.87 (m, β-C₁₈H₃₅, 4H), -1.27 (m, β-iBu, 4H), -2.41 to -2.53 (m, α-C₁₈H₃₅ and α-iBu, 12H)

UV/Vis (CHCl₃): λ_{max} = 670 nm (ε = 3.8 × 10⁵ M⁻¹ cm⁻¹)

2.2. Device fabrication

The indium–tin–oxide (ITO) coated glass substrates were cleaned by ultrasonication in toluene, acetone, and ethanol each for 15 min, dried with N₂, and cleaned with a UV–O₃ cleaner for 30 min. A thin layer (~40 nm) of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) (H.C. Starck, PH500) was spin-coated onto the cleaned ITO-coated substrate at 3000 rpm and was baked at 140 °C for 10 min in air. A ternary blend active layer (~200 nm) of P3HT:PCBM:dye was prepared from spin-coating on the PEDOT:PSS-coated ITO substrate at a spin rate of 600 rpm in an N₂-filled glove box. The wet film was slowly dried in a covered Petri dish for 3 h in the glove box. The ternary blend solution was prepared as follows: P3HT, PCBM, and dye were dissolved in *o*-dichlorobenzene at a concentration ratio of 20:20:1.7 mg mL⁻¹ and then the mixed solution was stirred at 40 °C overnight. In other words, the dye fraction was fixed to [SiPc] = 4.1 wt%, which is the optimized concentration as reported previously [19]. An electrode of Ca/Al layer

Table 1
Substituents of SiPc derivatives.

	R ₁	R ₂	R ₃
SiPc2	C ₂ H ₅ —	C ₂ H ₅ —	C ₂ H ₅ —
SiPc3	C ₃ H ₇ —	C ₃ H ₇ —	C ₃ H ₇ —
SiPc4	C ₄ H ₉ —	C ₄ H ₉ —	C ₄ H ₉ —
SiPc6	C ₆ H ₁₃ —	C ₆ H ₁₃ —	C ₆ H ₁₃ —
SiPcB18	C ₁₈ H ₃₇ —	(CH ₃) ₂ CH—	(CH ₃) ₂ CH—

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