Highly Fluorescent Blue-Emitting Materials from the Heck Reaction of Triphenylvinylsilane with Conjugated Dibromoaromatics

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Abstract: A new family of conjugated, highly photoluminescent blue-emitting organosilicon materials prepared from the Heck reaction of triphenylvinylsilane with various dibromoaromatics is described. The products are prepared in one high-yielding step (60–79%) from readily available starting materials. Their high photoluminescent quantum yields (67–98%) coupled with moderate glass transition temperatures (Tg, 69–138 °C) make them excellent candidates for active materials in organic light-emitting diodes (OLE-Ds).

Key words: Heck reaction, organosilicon, photoluminescent, OLEDs, vinyl silanes

Of the vast number of reports related to Heck chemistry,^{1–4} relatively few describe the cross coupling of aromatic halides with vinyl silanes.^{5–8} Of these reports, the formed Si-vinyl-aromatic containing molecules are often used as vinylating agents to replace the more toxic vinyltin compounds used in Stille coupling.^{9–12}

Our interest is to prepare new Si-vinyl-aromatic containing materials using Heck chemistry, as opposed to other more arduous protocols,^{13,14} and study their properties towards application in organic light-emitting diodes (OLE-Ds). We have previously reported the Heck coupling of octavinylsilsesquioxane with various monohalo functionalized aromatics and their resultant thermal, optical and device properties.^{15–17} As an extension of this work, we report here the Heck coupling of triphenylvinylsilane with various dibromoaromatics to form blue-emitting materials with excellent thermal and optical properties.

We chose triphenylvinylsilane as a precursor in this study for a variety of reasons. First, in order for a material to be considered useful for application in OLEDs, it generally must form amorphous thin films on the order of 25–75 nm. In the case of triphenylvinylsilane, the bulky triphenylsilyl groups provide a 'dumbbell-like' molecular shape that tends to suppress crystallization, as shown in Figure 1 for compound **3a**. Second, the bulkiness of the triphenylsilyl groups prevents double Heck addition across a single vinyl group, which has been found in other vinylsilane systems.^{12,16} Third, the formed linkage provides extended electron delocalization from the aromatic moiety to silicon through $\sigma^* - \pi^*$ interactions, that potentially provides materials with semiconducting properties and enhanced

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Figure 1 Space-filling model of 1,4-bis[(*E*)-2-(triphenylsi-lyl)vinyl]-benzene (**3a**) showing the 'dumbbell-like' structure that suppresses crystallization.¹⁹

photoluminescence.¹⁸ Lastly, triphenylvinylsilane is a commercially available, air- and moisture-stable solid.

As shown in Scheme 1, we employ bis(tri-*tert*-butylphosphine)palladium(0) {Pd[P(*t*-Bu)₃]₂} as catalyst, dicyclohexylmethylamine as base/HBr scavenger and toluene as solvent.²⁰ The reactions are run at 80 °C and are generally complete within 4–16 h – much more milder conditions than previously reported for vinylsilane-based Heck coupling.^{6–8} The reaction progress was monitored by TLC and MALDI-TOF. Product purification is very straightforward using precipitation and column chromatography techniques to produce target molecules in 60–79% yield. Product intermediate **2d** was prepared using known procedures.²¹

MALDI-TOF spectra show a very narrow distribution of peaks for all the compounds suggesting formation of single molecules respectively for all cases. A representative spectrum is shown in Figure 2 for compound **3e**. These results also confirm the complete suppression of double Heck additions across individual vinyl groups as no molecules with three or four additions of triphenylvinylsilane could be found. As a control experiment we reacted triphenylvinylsilane with a 2.2-fold excess of 1-bromo-4-fluorobenzene and <1% of the double Heck product was observed by GC-MS.

Thermal properties of the compounds were investigated using differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA), see Table 1. DSC indicates moderate to high glass transition temperatures (T_g) values ranging from 69–138 °C. The compounds are completely amorphous as indicated by no melting or crystallization events via DSC. TGA demonstrates the high thermal stability of these compounds with 5% mass loss in N₂ ranging from 350–451 °C.



Scheme 1 Heck coupling of triphenylvinylsilane with various dibromoaromatics.



Figure 2 Representative MALDI-TOF spectrum of compound **3e**, 9,10-bis[(*E*)-2-(triphenylsilyl)vinyl]anthracene.

Photoluminescence (PL) spectra were measured in toluene and peak emission values are reported in Figure 3 and Table 1. The materials in this study emit deep blue (**3a**–**c**), blue (**3d**), and sky blue (**3e**,**f**). PL quantum yields (Φ_{FL}) in toluene were calculated relative to 9,10-diphenylanthracene as standard. The calculated quantum efficiencies were relatively high, ranging from 67–98%, as shown in Table 1.



Figure 3 Photoluminscent spectra for compounds 3a-e.

In summary, a new family of highly fluorescent blueemitting, amorphous, and thermally stable organosilicon materials have been synthesized from a straightforward Heck-chemistry protocol using readily available starting materials. Further work in our laboratory will be directed towards evaluating these materials as emitters and charge transport materials in OLEDs.

Triphenylvinylsilane, 9,10-dibromoanthracene, 4-4'-dibromobiphenyl, 2,7-dibromo-9,9-dimethyl-9*H*-fluorene, 1,4-dibromobenzene, 4,7-dibromobenzo[*c*][1,2,5]thiadiazole, bis(tri-*t*-butylphosphine)-palladium(0) and dicyclohexylmethylamine were purchased from Sensient Imaging Technologies, Pacific Chem Source,

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Molecule	Mol. Wt.	Tg (°C) ^a	Td (°C) ^a	$\lambda^{abs}_{max}~(nm)^{b}$	λ^{em}_{max} , (nm) ^b	$\Phi_{FL}{}^{c}$
3a	647.0	75	366	308	395	0.81
3b	723.1	89	395	323	361	0.98
3c	763.1	106	392	342	372	0.88
3d	1169.7	138	451	374	421	0.85
3e	747.1	69	350	394	486	0.70
3f	705.0	85	367	399	481	0.67

Table 1 Thermal and Optical Properties of Compounds 3a-g

^a Measured in nitrogen.

^b Measured in toluene. PL spectra obtained by irradiating at respective UV/Vis absorbance maximum wavelengths.

^c 9,10-Diphenylanthracene used as standard.

Aldrich, Strem and TCI and used as received. All reactions were performed using Schlenk techniques in an argon atmosphere with anhydrous solvents.

All materials were characterized with ¹H NMR, ¹³C NMR and ²⁹Si NMR. All NMR analyses were carried out in CDCl₃ solvent on a Bruker DPX 400 MHz NMR. Tetramethylsilane (TMS) was used as an internal standard. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry (MALDI-TOF) was performed on a Bruker Autoflex MALDI Tandem TOF/TOF mass spectrometer. Dithranol was used as the matrix and silver trifluoromethanesulfonate (AgTFA) as the ion source when necessary. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Solution PL were measured in toluene. All thermal gravimetric calorimetry (TGA) analyses were carried out on a Thermal Analysis TGA 2050 module under N2 with a flow rate of 60 mL/min and a heating rate of 10 °C/min to 900 °C. Differential scanning calorimetry (DSC) analyses were performed under N₂ on a Thermal Analysis DSC 2920 module with a scanning rate of 10 °C/min. Photoluminescent quantum yields (PLQE, Φ_{FL}) were calculated based on a previously described method. 9,10-Diphenylanthracene was selected as reference for the PLQE measurement. The relative quantum efficiency was calculated according to the equation:

$$\Phi_{FL(sample)} = [A_{std}/A_{sample}][F_{sample}/F_{std}][n_{sample}/n_{std}]\Phi_{FL(std)}$$

where std is the 9,10-diphenylanthracene reference, A the absorption at the excitation wavelength, F the total integrated emission, n the refractive index of the solvent, and Φ_{FL} the quantum yield.

General Procedure for Heck Reaction 3a–g Procedure for the Preparation of 3a

Into a flame-dried 25-mL round-bottom flask were added triphenylvinylsilane 1 (0.3 g, 1.05 mmol, 1 equiv), 1,4-dibromobenzene 2a (0.53 mmol, 0.5 equiv) and bis(tri-t-butylphosphine)palladium(0) ${Pd[P(t-Bu)_3]_2}$ (5.34 mg, 0.01 mmol, 2 mol%). The flask was evacuated and refilled with argon three times. Anhyd toluene (15 mL) was added followed by nitrogen degassed dicyclohexylmethylamine (Cy₂NCH₃) (0.24 mL, 1.16 mmol, 2.2 equiv). The reaction was stirred for 24 h at 80 °C and monitored by TLC and MALDI-TOF. Upon completion, the reaction mixture was cooled to r.t. and filtered through a short Celite®/MgSO4 column to remove Pd particles and the amine hydrochloride. The filtrate was concentrated and precipitated into stirring acidified MeOH. The precipitate was filtered and purified via column chromatography using CH₂Cl₂hexane (3:1) as eluent. After chromatography, the solution was concentrated and reprecipitated into acidified MeOH and collected by filtration. Compound 3a was obtained as a yellow powder (60% yield).

Compound 3a

¹H NMR (CDCl₃): $\delta = 6.96-7.09$ (m, 4 H), 7.26–7.52 (m, 20 H), 7.59–7.66 (m, 14 H). ¹³C NMR (CDCl₃): $\delta = 123.47$, 126.99, 127.92, 129.61, 133.54, 134.42, 136.03, 148.26. ²⁹Si NMR (CDCl₃): $\delta = -16.66$. MS (MALDI; Ag⁺ adduct, 100%): *m/z* calcd: 755.16; found: 753.47. Isolated yield: 60%.

Compound 3b

¹H NMR (CDCl₃): $\delta = 6.73-7.01$ (m, 4 H), 7.30–7.48 (m, 14 H), 7.51–7.59 (m, 24 H). ¹³C NMR (CDCl₃): $\delta = 122.38$, 123.27, 127.08, 127.26, 127.95, 129.63, 134.48, 136.05, 139.33, 148.28. ²⁹Si NMR (CDCl₃): $\delta = -16.62$. MS (MALDI; Ag⁺ adduct, 100%): *m*/*z* calcd: 831.19; found: 829.59. Isolated yield: 72%.

Compound 3c

¹H NMR (CDCl₃): δ = 1.54 (s, 6 H), 6.96–7.09 (m, 4 H), 7.30–7.52 (m, 20 H), 7.59–7.66 (m, 16 H). ¹³C NMR (CDCl₃): δ = 27.25, 46.83, 120.45, 120.83, 122.35, 126.00, 126.33, 127.95, 129.62, 134.60, 136.10, 137.43, 149.14, 154.55. ²⁹Si NMR (CDCl₃): δ = -16.46. MS (MALDI; Ag⁺ adduct, 100%): *m/z* calcd: 871.22; found: 871.49. Isolated yield: 77%.

Compound 3d

¹H NMR (CDCl₃): δ = 1.54 (s, 9 H), 6.90–7.06 (m, 4 H), 7.35–7.44 (m, 50 H), 7.51–7.68 (m, 13 H). ¹³C NMR (CDCl₃): δ = 31.43, 42.53, 119.41, 120.11, 120.25, 123.06, 124.26, 124.49, 126.20, 127.10, 127.30, 127.66, 127.88, 129.52, 132.99, 134.76, 136.04, 144.51, 146.49, 148.33. ²⁹Si NMR (CDCl₃): δ = -16.54. MS (MAL-DI; 100%): *m/z* calcd: 1168.55; found: 1169.11. Isolated yield: 72%.

Compound 3e

¹H NMR (CDCl₃): $\delta = 6.85-6.99$ (m, 4 H), 7.42–7.51 (m, 18 H), 7.71–7.80 (m, 12 H), 8.25–8.27 (m, 8 H). ¹³C NMR (CDCl₃): $\delta = 125.27$, 126.13, 128.10, 128.57, 129.79, 134.41, 134.49, 135.14, 136.10, 147.01. ²⁹Si NMR (CDCl₃): $\delta = -16.91$. MS (MAL-DI; Ag⁺ adduct, 100%): *m/z* calcd: 855.19; found: 855.53. Isolated yield: 60%.

Compound 3f

¹H NMR (CDCl₃): $\delta = 6.90-7.04$ (m, 4 H), 7.35–7.51 (m, 20 H), 7.56–7.68 (m, 12 H). ¹³C NMR (CDCl₃): $\delta = 127.75$, 127.79, 127.89, 129.70, 130.18, 134.32, 136.13, 136.57, 144.05. ²⁹Si NMR (CDCl₃): $\delta = -16.55$. MS (MALDI; Ag⁺ adduct, 100%): *m/z* calcd: 813.12; found: 813.46. Isolated yield: 79%.

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