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Siloxane−Triarylamine Hybrids: Discrete Room Temperature Liquid Triarylamines via the Piers−Rubinsztajn Reaction

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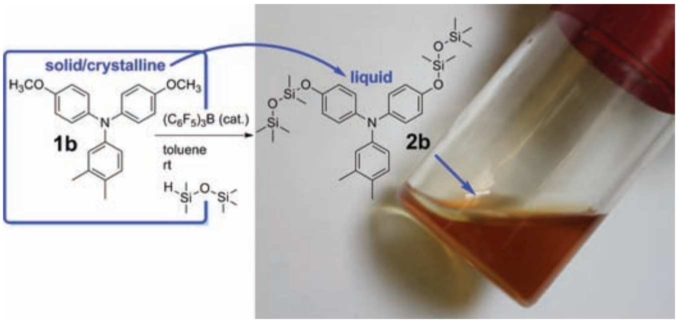
ABSTRACT



A series of room temperature liquid siloxane−triarylamine hybrids were synthesized using the Piers−Rubinsztajn reaction. These materials displayed well behaved electrochemical oxidation and low T_g's and were free-flowing liquids. The interaction between the Lewis acidic tris(pentafluorophenyl)borane catalyst and the Lewis basic starting triarylamine substrate was also investigated by steady state UV−vis spectroscopy and ^{19}F NMR.

Triarylamines are well studied *p*-type semiconducting materials that have been used in many organic electronic devices such as organic light emitting diodes (OLEDs), photovoltaics (OPVs), organic field effect transistors (OFETs), and xerographic photoreceptors (OPRs) among others.[1] Their synthesis is normally accomplished by palladium or copper-catalyzed amination reactions starting from anilines or diarylamines and aryl halides. These powerful synthetic tools allow for the synthesis of many different complex triarylamine based structures that display a variety of interesting and controllable properties and functions.[2] Recently, the use of liquid triarylamines has been explored for application in OLEDs and dye sensitized solar cells (DSSCs). Specifically, *N*-(2-ethylhexyl)carbazole has shown utility as a host material having superior properties to its polymeric analog (polyvinylcarbazole).[3] Tris(4-methoxyethoxyphenyl)amine, also a liquid, has been shown to be an alternative to the more widely

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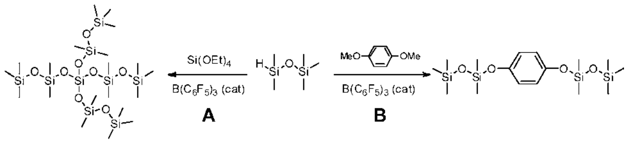
used I^-/I_3^- redox couple in a DSSC. The resulting DSSC had a reported efficiency of 2.4% under AM1.5 illumination.[4] However, in each of these cases, the arylamine structure is not generally amenable to synthetic variation. As a result, the physical (melting point, viscosity, solubility/dispersibility) and electronic properties (oxidation potential) of the arylamine cannot be systematically varied. Access to new synthetic methods that lead to a broader range of liquid arylamines is therefore necessary.

The Piers−Rubinsztajn reaction has been shown to be a powerful way to construct complex discrete siloxane architectures in an efficient manner.[5] This reaction uses the strong Lewis acid tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) to catalyze the reaction between Si−H and Si−O−R groups (where R = H, Me or other alkyl, $R_3SiH + R'OSiR''_3 \rightarrow R_3SiOSiR''_3 + R'H$, Scheme 1A).[6] This chemistry typically occurs very rapidly and is done under nonaqueous conditions. Crucial to the utility of the process is the fact that silicones do not undergo metathesis/redistribution in the presence of this Lewis acid.[5b] As well, the borane catalyst is generally easy to remove and the byproduct is either hydrogen or volatile hydrocarbon gases (such as methane) either of which rapidly leave the solution during reaction or under gentle vacuum. Using this chemistry, the synthesis of many complicated and otherwise inaccessible siloxane structures and other chemical derivatives can be achieved.[7]

Scheme 1. Partial Scope of the Piers−Rubinsztajn Reaction



In addition to the synthesis of Si−O−Si bonds for discrete siloxane architectures, this chemistry has also been shown to work between Si−H bonds and aryl-hydroxyl groups and aryl-methoxy groups to form aryl−O−Si bonds (Scheme 1B).[8]

In this communication we describe a series of free-flowing room temperature liquid siloxane−triarylamine hybrid compounds that were prepared using the Piers−Rubinsztajn reaction. In this study, pentamethyldisiloxane (−PMDS) was chosen as a prototypical reactive silicone because it is a pure and discrete compound, a liquid, inexpensive and readily available. Para-methoxy functionalized triarylamines were chosen as substrates due to their synthetic accessibility and their known physical and electronic properties.[2b]

Each precursor *para*-methoxy-triarylamine can be synthesized in a single step using well established Buchwald−Hartwig coupling conditions[9] by the reaction between 4-bromoanisole and bis(3,4-dimethylphenyl)amine, 3,4-dimethylaniline, or *p*-anisidine giving triarylamines **1a**−**c**, respectively. Each methoxy functionalized triarylamine was subsequently reacted with PMDS in the presence of tris(pentafluorophenyl)borane. In a typical procedure, the triarylamine was dissolved in toluene (10 wt %) which contained a catalytic amount of tris(pentafluorophenyl)borane (1 mol %) at room temperature in an open vessel. To this, PMDS was added dropwise. There is a short induction time following which the rapid evolution of gas occurs (methane in this case): *Safety Note - the evolution can be vigorous, and the addition rate of the silane should be adjusted accordingly*. Reactions were worked up by the addition of ~0.5 g of basic alumina, which was allowed to stir for an additional 20 min within the reaction vessel to capture the borane catalyst. The reaction solution was filtered, and the solvent and excess pentamethyldisiloxane were simply removed by rotary evaporation. A general reaction is illustrated in Scheme 2. The isolated yields for these reactions typically exceeded 90%. We found that no further purification of these compounds was required after removal of excess PMDS and boron catalyst (as shown by HPLC and ^1H NMR analysis). The ^1H NMR analysis is somewhat complicated by the observation of long-range coupling. All three siloxane−triarylamine hybrid compounds were isolated as pale yellow, free-flowing liquids. Compounds **2b** and **2c** had

Scheme 2. Synthesis of Siloxane−Triarylamine Materials

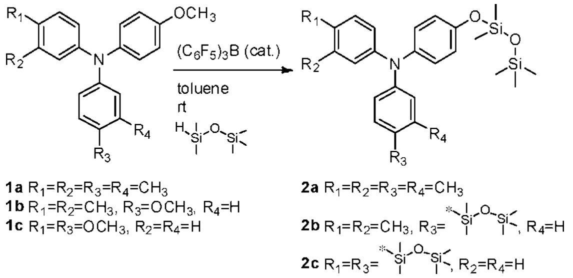


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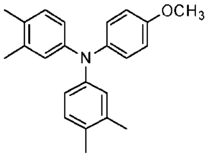
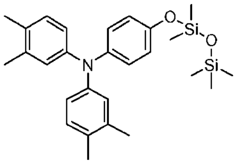
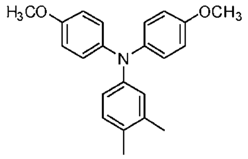
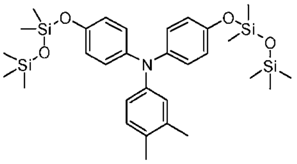
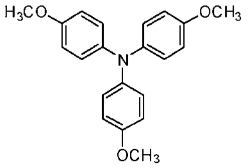
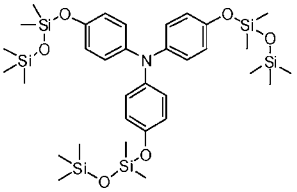
Table 1. Characterization Data for Compounds **1a−c**[a] and **2a−c**

triarylamine	T_m (°C)[a]	T_g (°C)[a]	$E_{1/2ox}$ (mV)[†]	siloxane-triarylamine	T_m (°C)	T_g (°C)	$E_{1/2ox}$ (mV)
1a  	122	4	735	**2a**  	-	-45	761
1b  	86	1	690	**2b**  	-	-50	739
1c  	98	8	654	**2c**  	-	-63	713

[a] Taken from ref 2b.

viscosities similar to that of a 5130 g/mol weight averaged PDMS standard, whereas **2a** was similar to a 24 800 g/mol standard. Precise measurements are underway.

Each of the compounds **2a−c** was characterized by differential scanning calorimetry (DSC) to establish the effect of siloxane substitution on the arylamine and to observe any thermal transitions which may exist (Table 1). DSC analysis was performed by first rapidly cooling each liquid to −80 °C. Each sample was then subsequently heated to room temperature, back down to −80 °C and finally back to room temperature all at a rate of 10 °C/min. Sharp glass transitions (T_g) were observed in all cases in each of the heating cycles. No other thermal transitions were observed for these compounds (complete DSC curves are provided in the Supporting Information). It can be seen that addition of the PMDS group has a strong effect on the physical properties of the triarylamines. The normally crystalline starting methoxy-triarylamines (**1a−c**) are converted to liquids with very low glass transition temperatures ranging from −45 to −63 °C. It is observed that increasing the number of PMDS chains decreases the glass transition temperature. In no cases were other thermal transitions including crystalline transitions observed.

Each siloxane−triarylamine hybrid was also characterized by cyclic voltammetry (CV) to determine the effect of PMDS substitution on the electrochemistry of the compounds. Each was run under identical conditions to those for compounds **1a−c**, and their results were compared.[2b] CV was performed in dichloromethane with $(Bu)_4NClO_4$ as a supporting electrolyte. Each compound was scanned from −300 to +1100 mV and back to −300 mV at 50 mV/s. Each was cycled through this range four times in total. Decamethylferrocene was used as an internal standard, and all data is corrected to its published half wave potential.[10] The results are summarized in Table 1. Siloxane−triarylamine hybrids (**2a−c**) have very similar electrochemical behavior to that of the methoxy substituted triarylamines **1a−c** with a single reversible oxidation event. We observed that the halfwave oxidation potential ($E_{1/2}$) for compounds **2a−c** decreases with increasing PMDS substitution. This implies that PMDS is an electron-donating group.[11] However, based on the comparison to the $E_{1/2}$ for compounds **1a−c** we can conclude that the PMDS moiety is a weaker electron-donating group than methoxy.

The accepted mechanism for the Piers−Rubinsztajn reaction initially involves the formation of a reversible complex between the Si−H of the silane and the boron center of the Lewis acid catalyst as a key intermediate step.[6b] It was anticipated that the strong Lewis acid used herein[12] could competitively bind to the substrate triarylamine, which is a weak Lewis base.[13]

The efficiency of the process described herein suggests there is little interaction between tris(pentafluorophenyl)borane and the triarylamine substrate. However, if a Lewis acid|base interaction took place, it would likely involve the removal of an electron from the triarylamine resulting in the brightly colored radical cation of the triarylamine thereby allowing for detection of even trace amounts of interac-

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tions.[14,15] Thus UV−vis spectra of triarylamine **1c** were taken between 300 and 2000 nm with varying equivalents of tris(pentafluorophenyl)borane in dilute solutions of toluene (0.0298 mol/L). Looking at the visible region of the spectrum, a very weak absorbance centered at 742 nm can be observed (Figure 1). This peak increased in intensity in a nonlinear fashion with increasing amounts of tris(pentafluorophenyl)borane. A chemically oxidized solution of triarylamine **1c** with 0.5 equiv of antimony(V) chloride ($SbCl_5$) was also prepared. It is well-known that the oxidative action of $SbCl_5$ on a (tri)arylamine produces the radical cation via a single electron transfer.[16] The UV−vis spectrum of the mixture of **1c** and $SbCl_5$ overlaps with the position and has the same peak shape observed for the mixtures of **1c** and tris(pentafluorophenyl)borane (Figure 1). It can thus be concluded that there is some level of interaction between tris(pentafluorophenyl)borane and the triarylamine and that the interaction results in the formation of a radical cation|radical anion pair. The absorbance at 742 nm was extremely weak compared to its primary absorption band at 298 nm. Given the extinction coefficient of a (tri)arylamine radical cation is known to be very high[16] relative to the neutral compound, the spectra suggest that **1c** and tris(pentafluorophenyl)borane are in an equilibrium shifted far toward dissociation. To confirm this, ^{19}F NMR was performed on an equimolar mixture of **1c** and tris(pentafluorophenyl)borane.[17] No change in the ^{19}F chemical shifts of tris(pentafluorophenyl)borane was observed thereby confirming the equilibrium is shifted far toward dissociation.

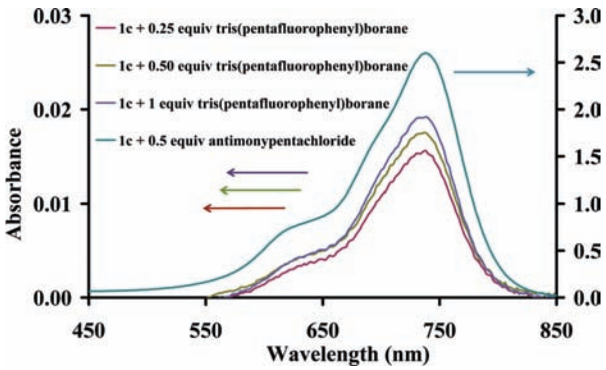

Figure 1. Steady state UV−vis absorbance spectra of **1c** upon addition of 0.25, 0.5, and 1 equiv of tris(pentafluorophenyl)borane. Also shown is **1c** oxidized with 0.5 equiv of $SbCl_5$ for reference.

In summation, the functionalization of triarylamines with discrete silioxane chains under Piers−Rubinsztajn conditions (tris(pentafluorophenyl)borane catalysis) has been shown to drastically change their physical properties. The result is a sample of three free-flowing room temperature liquid siloxane−triarylamine hybrids. Any Lewis acid/Lewis base interaction between the arylamine and borane catalyst is weak such that free catalyst is available to interact with the hydrosilane and initiate the Piers−Rubinsztajn process. We believe that this synthetic strategy will facilitate further application of liquid arylamines in optoelectronic devices.

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Supporting Information Available: Experimental data, NMR spectral data, CV data and DSC data for compounds **1a**−**c** and **2a**−**c**. ^{19}F NMR spectra for mixtures of **1c** and tris(pentafluorophenyl)borane. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) ^{19}F NMR was performed in deuterated benzene (C_6D_6). All peaks are referenced to an external standard of BF_3·Et_2O. Detailed ^{19}F spectra are included in the Supporting Information.