Heck coupling of haloaromatics with octavinylsilsesquioxane: solution processable nanocomposites for application in electroluminescent devices

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A new solution processable nanocomposite material has been prepared *via* the Heck coupling of octavinylsilsesquioxane with a selected bromoaromatic hole transport compound. Resultant electroluminescent devices show an 18% improvement in external quantum efficiencies over their small molecule analogues.

Organic light emitting diodes (OLED) are a highly targeted area of technology because of their expected utility in flat panel displays.[1] From a materials perspective, the past decade has witnessed much debate over which family, small molecules or polymers, is best suited for OLEDs.[2,3] Small molecules can be highly purified and vacuum deposited in multi-layer stacks, both important for display lifetime and efficiency. However, vacuum deposition techniques require costly capital equipment, a limitation to practical display size, and significant problems with achieving full color displays at high volume using masking technologies.[4] Polymers are generally of lower purity than small molecules but can access larger display sizes and full color at much lower costs *via* solution-based deposition techniques.[5,6] In this communication, we report a nanocomposite material based on a silsesquioxane architecture that combines the advantages of both small-molecule and polymer approaches to OLEDs. The material contains a spherical "silica" core with a hole transport functionalized periphery. The resulting materials offer numerous advantages for OLEDs including: amorphous properties, high glass-transition temperatures (Tg), low polydispersity, solubility, and high purity *via* column chromatography. Initial OLED device performance data is presented, using a hole transport functionalised nanocomposite, that shows an 18% improvement over their molecular counterparts.

We are interested in using silsesquioxanes as a platform technology for solution processable nanocomposites. Previous work has shown that liquid crystalline nanocomposites can be prepared by linking organic mesogens to a silsesquioxane core using an adjustable flexible link.[7–10] This allowed for the mesogens to organize the nanocomposite materials into various liquid crystalline phases. In the case of OLED technology, liquid crystalline or other organized regions are undesirable as they have been shown to contribute to charge trapping and a general decline in device performance.[11] Others have used silsesquioxanes in light emitting devices as pendent/end groups on polymers, and as cores for star-like polymers.[12–14] Our goal was to design silsesquioxane based nanocomposites that combined the organic molecular electronic component with the silsesquioxane core using a rigid link.[15] One candidate core material was the commercially available octavinylsilsesquioxane (OVS) wherein the vinyl group could undergo Heck coupling with mono haloaromatics to form a rigid Si–vinyl–aromatic link. However, Heck reactions on vinyl silanes are quite uncommon and usually limited to iodo and bromo aromatics.[16–19] Furthermore, recent studies on the chemistry of vinyl silanes were directed towards Stille-like coupling and their use as *vinylating* agents to replace the more toxic vinyltin compounds.[20] Using recent advances in Heck chemistry,[21] we have been able to couple haloaromatics, including chloro, with OVS.

For a comparative study of the OVS based nanocomposite for use in OLEDs, we selected *N*4-(9,9-dimethyl-9*H*-fluoren-7-yl)-*N*4′-(9,9-dimethyl-9*H*-fluoren-2-yl)-*N*4,*N*4′-diphenylbiphenyl-4,4′-diamine (FL03), shown in Fig. 1 as the hole transport moiety as it has been shown to have excellent hole transport properties for OLEDs.[22]

Therefore, a mono brominated version was synthesized [*N*4-(2-bromo-9,9-dimethyl-9*H*-fluoren-7-yl)-*N*4′-(9,9-dimethyl-9*H*-fluoren-2-yl)-*N*4,*N*4′-diphenylbiphenyl-4,4′-diamine (Br-FL03)] that

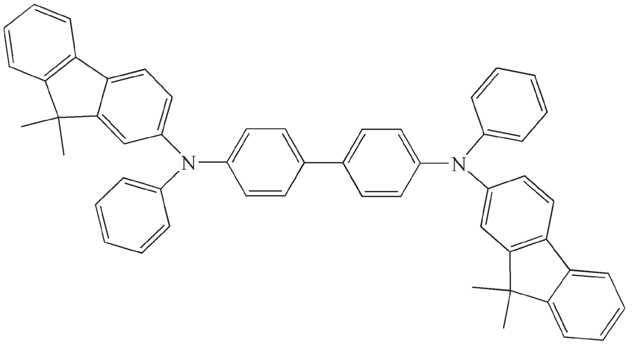

Fig. 1 Hole transport compound *N*4-(9,9-dimethyl-9*H*-fluoren-7-yl)-*N*4′-(9,9-dimethyl-9*H*-fluoren-2-yl)-*N*4,*N*4′-diphenylbiphenyl-4,4′-diamine (FL03).

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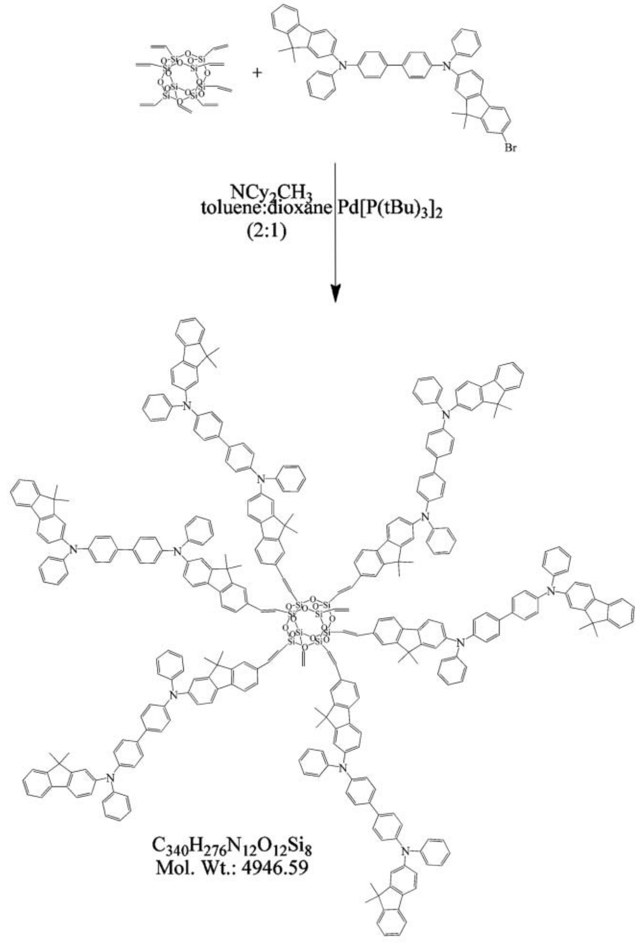
could be covalently attached to the OVS core. Reactions performed using OVS with 6 equivalents of Br-FL03 yielded FL03-OVS in >75% yield, see Scheme 1.

The reaction was carried out at 70 °C for 24 h using a 2 : 1 toluene : dioxane solvent mixture, bis(tri-*tert*-butylphosphine)-palladium(0) [Pd[P(tBu)$_3$]$_2$] (1.0 mol%) as catalyst, and dicyclohexylmethylamine as base/HBr scavenger. The reaction was monitored by TLC, size exclusion chromatography and visually by the precipitation of dicyclohexylmethylaminehydrobromide by-product. Additionally, UV light was used to qualitatively observe the appearance of intense blue photoluminescent emission during the course of the reaction. On completion, the reaction mixture was precipitated into methanol to produce a fine pale yellow powder that was collected by filtration. The powder was then dried, re-dissolved in minimal dichloromethane, filtered through a 1 μm filter into stirring methanol and again collected by filtration. Final purification was achieved by column chromatography using hexanes : ethyl acetate (10 : 1) followed by dichloromethane. Even after multiple dissolutions and precipitations, a black material remained at the top portion of the column during purification. This material is assumed to be Pd particles formed during the course of reaction that are known to promote detrimental properties to subsequent solution processed OLEDs.[23] In the case of light emitting polymers where syntheses involve Ni and Pd catalysis, the purification process generally involves the multiple precipitation technique, as high molecular weight polymers are difficult to purify by column chromatography. Therefore the ability to column purify solution processable materials designed for application in OLEDs, is very important.

Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) analysis revealed silsesquioxane cores with 3–10 substitutions per Fig. 2. The propensity for substitutions beyond 6, especially 9 and 10, is quite surprising considering steric factors. The presence of 9 and 10 substitutions indicates double Heck reactions across vinyl groups which is quite uncommon in traditional styrene and methacrylate based Heck reaction studies.[24] This suggests that a mono-substituted vinylsilane group is more reactive towards subsequent Heck additions. We are currently studying this observation in more detail.

Size exclusion chromatography (SEC) in THF revealed a single peak with a low polydispersity of 1.05 suggesting no reactants, by-products or core breakdown. As the hydrodynamic volumes of the 3–10 substituted species are quite similar, the GPC is unable to separate.[25]

Differential scanning calorimetry (DSC) of FL03-OVS indicates a high glass transition temperature (*T*g) of 193 °C and no indication of melting or crystallization up to the decomposition point. This is a 73 °C enhancement over the *T*g of FL03. Fig. 3 shows the thermal gravimetric analysis (TGA) in air and reveals very high thermal stability, 5% mass loss at 465 °C, and ceramic yields (to SiO_2) slightly lower than expected (8.3% *vs.* 9.7%) suggesting an average substitution of 7.2. This is likely due to lower substituted species (1–3) that are partially soluble in



Scheme 1 Synthesis of FL03-OVS.

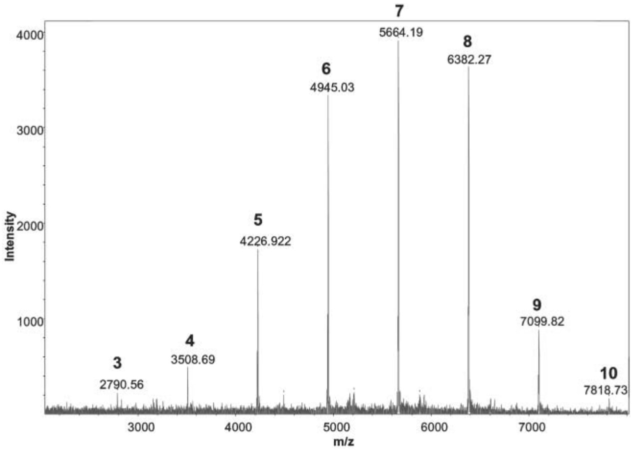


Fig. 2 MALDI spectrum of FL03-OVS.

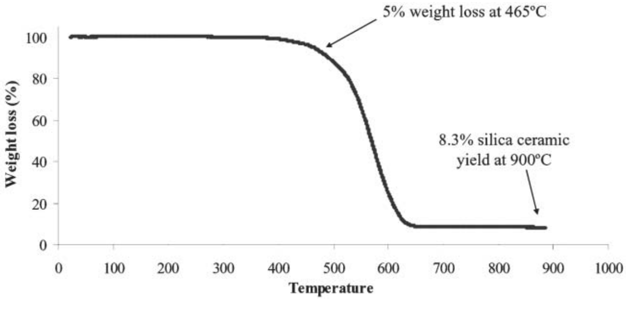


Fig. 3 TGA spectrum of FL03-OVS in air.

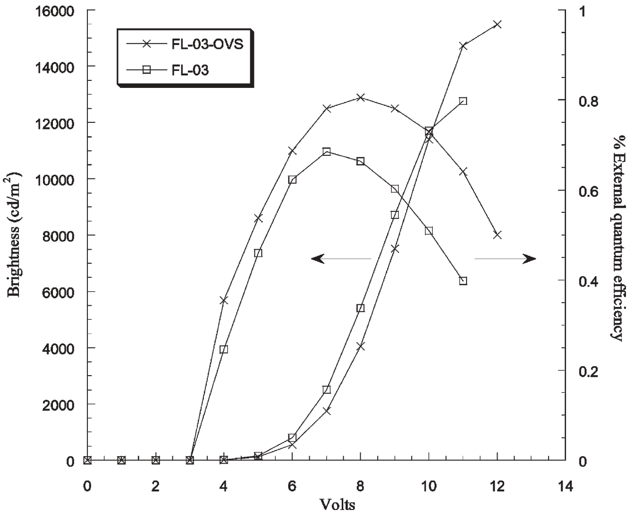


Fig. 4 OLED brightness and external quantum efficiency *vs.* voltage using FL03-OVS and FL03.

methanol and lost during the purification process. MALDI-TOF and TGA analysis of samples isolated by extraction using separatory funnel techniques followed by column chromatography show a larger proportion of lower substituted silsesquioxane (2–5), and ceramic yields closer to materials with 6 substitutions.

Thin film and solution (toluene) photoluminescent spectra have nearly identical shapes and show $PL_{\max}$ of 430 nm and 434 nm respectively, suggesting no tendency towards aggregation in the solid state.

To demonstrate the potential of these nanocomposite materials in organic electronic applications, OLEDs were prepared using molecular FL03 *vs.* FL03-OVS as hole transport layers in standard undoped tris(8-hydroxyquinolinato) aluminum (Alq_3) based devices. Devices for each material were prepared under identical conditions and results are shown in Fig. 4.[26]

Devices of each material show similar turn-on voltages (3 V), while FL03-OVS based devices show higher maximum brightness (15 495 cd m^{-2} *vs.* 12 755 cd m^{-2}), and higher external quantum efficiencies (0.80% *vs.* 0.68%). We have observed similar trends with other hole transport based OVS nanocomposites.

In conclusion, reported here is a new class of solution processable amorphous nanocomposite materials based on silsesquioxane cores with many attractive properties for application in organic light emitting diode (OLED) technology including: ease of synthesis, high glass-transition temperatures (Tg), high solubility, good film-forming properties, low polydispersity, and high-purity *via* column chromatography. Preliminary OLED device results using hole-transport functionalized nanocomposites show an 18% improvement in efficiency *vs.* their small molecule analogues. Future work in this area will explore cores derivatised with other organic electronic functional groups such as electron transport, emissive, absorptive, and conductive for application in OLEDs, organic photovoltaics, and organic thin film transistors respectively.

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26 In a typical experiment, glass substrates coated with indium tin oxide ITO were cleaned ultrasonically in sequential steps using acetone, methanol and finally isopropyl alcohol. Prior to loading in the vacuum deposition system the substrates were plasma ashed to remove any organic contaminants on the ITO surface. Both materials were spin coated from chloroform 10 mg mL^{-1} to yield a thickness of 40 nm. The substrates were then loaded into a vacuum chamber and a. 60 nm thick light-emitting layer of Alq_3 was deposited on top of the hole transport layer followed by 12 nm of an Al–Li alloy (98.5 : 1.5) and 150 nm Al. Devices were then quickly encapsulated in the presence of barium oxide getter, tested and characterized in ambient conditions.