Systematic Improvement in Charge Carrier Mobility of Air Stable Triarylamine Copolymers

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A combination of improved semiconducting polymer molecular design[1−5] and fabrication techniques[6] has resulted in recent demonstrations of both p- and n-type charge carrier mobilities exceeding application relevant values of 0.01 $cm^2/(V\ s)$ in field effect transistor devices, fabricated and measured in air over extended periods. However, even in instances where "reasonable" ambient stability is reported, it is often the case that devices driven under high current density (saturation) conditions or where the transistor architecture is bottom gate, with the semiconductor film exposed to ambient conditions, suffer from operational and even storage instabilities, leading to large initial carrier mobilities deteriorating to significantly lower values over short periods.[7] Over typical operation lifetimes, the mobility often degrades by over an order of magnitude.[2] Additionally, high mobility devices may also require both surface treatment and prolonged thermal annealing steps to optimally orient and order at the molecular and domain length scales.[8] These additional processing steps compromise the requirement of ease of fabrication. Clearly there is still demand for high performance, fully air stable polymers that when deposited from solution do not require further treatment to obtain optimal performance and have the flexibility to be employed in any device architecture.

In this report, we demonstrate that incorporation of bridged phenyl units, specifically fluorene and indenofluorene,[9,10] substantially improves the charge carrier mobility of triarylamine polymers, by almost an order of magnitude, while still retaining the excellent stability of aryl amine semiconducting polymers.[7] Planar, conjugated aromatic repeat units incorporated into semiconducting polymer backbones have previously been shown to promote highly ordered and oriented microstructures. In most cases, extensive intermolecular π-stacking arises from the assembly of the coplanar polymer conformation which contributes to enhancing in-plane transport.[11] A common molecular template for organization is the thiophene or fused arylthiophene repeat unit. The incorporation of conjugated thiophenes in a polymer, however, often leads to sensitivities to ambient oxygen, moisture, or light, often attributed to the high electron density, reactive diene functionality, and long wavelength optical absorption exhibited by the thiophene units.[12] The carbon bridged phenylene units fix coplanarity between adjacent phenylene rings, optimizing backbone conjugation, as also shown in previous work on oligomeric systems,[13] as well as increasing polymer persistence length, while reducing backbone conformation rotational disorder. This improved coplanarity is believed to be a primary reason for the observed improvements in charge carrier mobility on incorporation of the bridged units.

Methyl substituted phenylamine polymers have been shown to have excellent ambient photo and electrical stability.[7] The presence of the amine nitrogen in the backbone acts to prevent efficient delocalization of electrons between adjacent phenyl units, thus limiting the effective conjugation length and resulting in low lying HOMO energy levels and excellent oxidative stability. DFT calculations suggest an equilibrium torsion angle of 36° between successive units. The nonplanar, rotationally free and large linkage angle backbone however prevents optimal intermolecular π-electron delocalization, leading to an amorphous microstructure and relatively low charge carrier mobility in comparison to the polymers referred to earlier. Further thermal treatment of the as-cast thin films does not result in an improvement in charge carrier mobility, as there is no microstructural ordering on annealing; thus a time-consuming processing step can be circumvented. The design strategy employed is to introduce low electron density, bridged biphenyl and triphenyl units which will extend the backbone conjugation without significantly affecting the HOMO energy level. Both dialkylated fluorene and indenofluorene repeat units were incorporated in a 1:1 stoichiometry. In fact DFT calculations suggest that, since the fluorene and indenofluorene units have lower HOMOs than TAA, their inclusion in the polymer backbone further stabilizes positive charges. DFT calculations were carried out on the polymers with geometries optimized using the hybrid density functional B3LYP and a double split Pople basis set with extra polarization (6-31 g*). Calculations were performed on oligomers of lengths 1, 2, 3, 4, and 5 (counting a TAA unit and a PF8 or PIF8 unit as a unit, Figure 1) at which point the HOMO energy was found to change by less than 10 meV. Aliphatic side chains were removed from the polymer prior to computation.

All three polymers were synthesized via Suzuki polycondensation protocol, optimized to obtain a number average molecular weight in
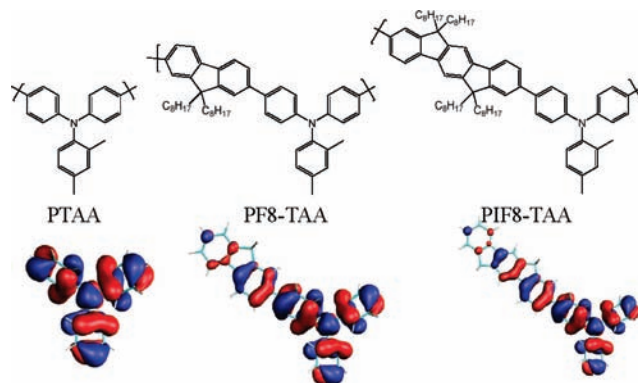
Figure 1. Polymer molecular structure and highest occupied molecular orbital distribution.

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the 25−100 kDa range. Although the molecular weight is not identical for all polymers, we do not expect a strong molecular weight dependence on electrical properties, as the number average molecular weight is above 15 kDa in all cases, the end group density will be low, and we should be in a plateau region for electrical properties. The catalyst chosen was $Pd_2(dba)_3/(o\text{-}tol)_3P$, a K_3PO_4 base, and Aliquat 336 was employed as the phase transfer catalyst in a toluene/1,4-dioxane/water solvent. Full experimental and characterization details are provided in the Supporting Information. PTAA was obtained by the A-B polycondensation of N-(4-bromophenyl)-4-(4,4,5,5-tetram-ethyl-1,3,2-dioxabo-rolan-2-yl)-N-(2,4-dimethylphenyl)benzenamine monomer, whereas both copolymers were formed from an AA BB Suzuki cross coupling condensation from the dibromotriarylamine and the pinacol ester boronates of the bridged phenyl repeat units. All polymerizations proceeded in good yield; the polymers were purified by washing via Soxhlet extraction with methanol, acetone, and iso-hexane. The trace amount of palladium salt was removed by treating the polymer solution in chloroform with sodium diethyldithiocarbo-mate. The polymer structures were characterized by ^1H and ^{13}C NMR spectroscopy and element analysis. The weight-average molecular weights (M_w) were determined by GPC versus polystyrene, and results are summarized in Table 1. All polymers are soluble in organic solvents such as chloroform, THF, and chlorobenzene, as well as more printing friendly solvents such as toluene and xylene. The incorporation of the dialkyl carbon bridging functionality and its out of plane projection preserves the good solubility of the triaryl amine unit. No first-order thermal transitions could be observed by differential scanning calo-rimetry, and preliminary NEXAFS and GIXRD data indicate an absence of measurable orientation or order in thin films. Additionally, annealed thin films appear to exhibit no birefringence under crossed polarizers.

Table 1. Polymer Properties

polymer	M_w/M_n (kDa)	HOMO (PESA) (−eV)	HOMO (DFT) (−eV)	charge carrier mobility ($cm^2/(V\ s)$)
PTAA	96.4/45.5	5.2	4.6	4×10^{-3}
PF8-TAA	52.9/27.9	5.4	4.8	2×10^{-2}
PIF8-TAA	25.4/15	5.5	4.7	4×10^{-2}

An experimental estimation of the HOMO energy levels of the polymers by Photo Electron Spectroscopy in Air (PESA),[14] summarized in Table 1 (shown in full in the Supporting Informa-tion), confirms high HOMO energy levels. This was expected to enhance stability to electrochemical oxidation in the presence of ambient oxygen and humidity.[15]

Bottom-contact, top-gate (and bottom-gate) architecture field effect transistor devices were fabricated with the polymer semiconductors deposited from solution. As cast, hole mobilities were calculated from the transfer characteristics using a standard thin film model. PTAA devices showed a mobility of $\sim4 \times 10^{-3}$ $cm^2/(V\ s)$. This was improved by a factor of 5 to 0.02 $cm^2/(V\ s)$ by the introduction of the fluorene unit and further increased to 0.04 $cm^2/(V\ s)$, for the indenofluorene copolymer (transfer characteristics shown in Figure 2b) with an ON/OFF ratio in excess of 10^6. It is speculated that the increase in polymer backbone planarity and persistence length in the copolymers leads to improvement in the intramolecular π-orbital overlap as well as improving the local structural organization, resulting in the measured increase in hole mobilities. No evidence of thin film crystallinity could be observed for any polymer semiconductor. Devices were stored in ambient conditions and periodically measured over a period of several months. Figure 2b illustrates ON and OFF currents, mobilities
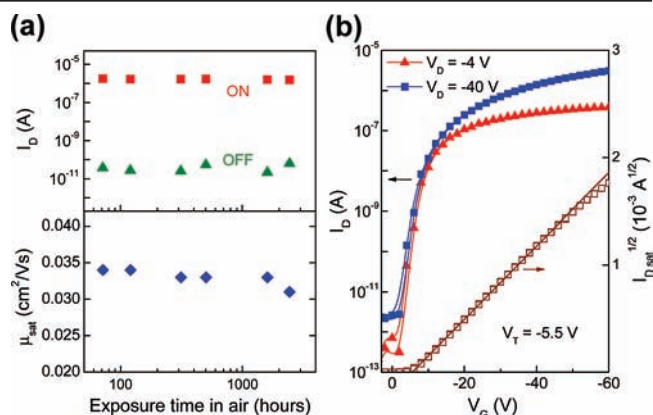
Figure 2. (a) (Top) Periodic ON and OFF currents and (bottom) charge carrier mobility measurements on ambient devices stored in air over a period of ∼3 months. (b) Transfer characteristics of PIF8-TAA copolymer with $L = 30\ \mu m$, $W = 1000\ \mu m$, corresponding to a mobility of 3.8×10^{-2} $cm^2/(V\ s)$.

measured over several weeks in a top gate device. Both top and bottom-gate devices, where in the latter case the semiconductor is directly exposed to ambient, showed that, within experimental measurement accuracy, there was no change in electrical performance. As a perspective, even the relatively stable polymer pBTTT would show a two orders of magnitude drop in ON current under the same conditions.[2] In summary, incorporation of the bridged triphenyl repeat unit, indenofluorene, as an alternating copolymer with triarylamine has been shown to provide high performing amorphous, solution process-able semiconducting polymers, suitable for printing large area electronics.

Supporting Information Available: Synthesis of PTAA, PF-TAA, PIF-TAA; PESA data; transfer and output transistor characteristics; air stability data, UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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