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Control of Charge-Carrier Mobility via In-Chain Spacer Length Variation in Sequenced Triarylamine Functionalized Polyolefins

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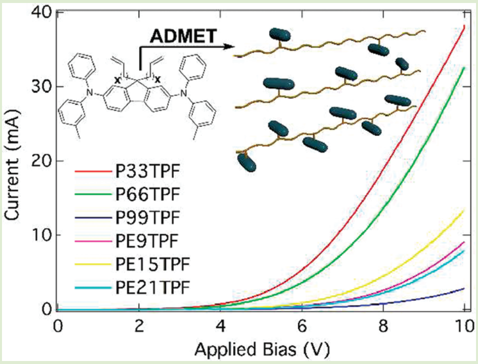
Supporting Information

ABSTRACT: A set of six perfectly regioregular pendant 2,7-bis(phenyl-*m*-toluylamino)fluorene (TPF) functionalized polyolefins for use as charge transporting materials in polymer light emitting diodes (PLEDs) were prepared and characterized. Synthesis of these materials is straightforward, requiring only three or four steps, depending on the polymer, and final isolated yields over all steps combined were greater than 40% in all but one case. Most notably, these materials exhibit charge-carrier mobilities that can be controlled over 3 orders of magnitude by variation of the number of intermediary carbons (spacer length) between the pendant TPF groups. The range of hole mobilities encompasses the electron mobilities of common electron transport materials/emitters such as Alq_3 and PBD, thus, affording the opportunity to fabricate electroactive polyolefin based PLEDs with well matched charge-carrier mobilities and improved performance. We believe this approach to charge-carrier mobility control in electroactive materials could be easily extended to other aryl systems with different HOMO−LUMO levels for energy level and mobility matching with various emitters.



Due to their easy solution processing and mechanical flexibility/durability, polymer light emitting diodes (PLEDs) are well suited for emissive lighting and large area displays. However, their performance is presently much lower than that of their inorganic or molecular counterparts.[1,2] Electroactive materials for PLEDs may be fully conjugated polymers (CPs; A of Figure 1) or polymers containing discrete π-functional groups either in the main chain (B) or pendant to it (C).[3−12] Type D materials, regioregular electroactive polymers, which comprise a special subclass of type C but with π-functional groups at defined intervals, are the focus of this paper.

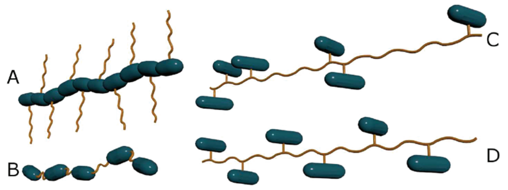


Figure 1. Schematic of electroactive polymer architectures.

Of particular importance to the performance of any LED is the balance of hole and electron transport, such that recombination occurs near the center of the device, thereby avoiding quenching near the electrodes. Charge balance and location of the recombination zone is directly related to the hole and electron mobilities of the materials used.[13−18] Furthermore, because the mobility of holes in organic materials is often much higher than that of electrons,[18] achieving balanced charge transport may necessitate the use of materials with intentionally reduced hole mobilities. In fact, in a recent report, Chen and co-workers applied precisely this concept to achieve very high efficiency in blue electrofluorescent LEDs.[19]

A number of materials with charge-carrier mobilities suitable for PLED hole transporting layers or hosts are available, usually triaryl amines, some reports of controlled mobility via modifications of CP side chains exist,[16] and control of charge-carrier mobilities in LED host layers has been achieved by blending small molecules into polymers.[20,21] In the latter case, device stability and performance is known to suffer as a result of phase separation,[20] which can be mitigated by copolymerizing the transporter species;[22] however, as new transporters become available, preparing new polymerizable derivatives thereof and optimizing copolymer ratios may prove too laborious. Therefore, single transporter based polymers with tunable mobilities that can be matched directly to the emitter's mobility are advantageous. However, to the best of our knowledge, polymeric systems in which mobility has been measured and shown to be tunable over a range via modification of an insulating or otherwise inert polymer backbone, rather than modification of the charge transporting moiety or CP side chains, have not been well studied. From a device optimization perspective, such

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materials offer the advantage that the energy levels of the species involved in transport remain constant. Thus, materials can be energetically matched for charge injection/transfer, followed by independent optimization of charge-carrier mobility. On the other hand, optimization of mobilities via use of structurally different charge transporting chromophores (e.g., NPD vs DCBP) complicates device design because differences in both mobility *and* energy levels (which directly affect charge injection barriers) must be simultaneously considered and may necessitate employment of more complex device architectures.[13,23]

In a manuscript recently accepted by *Macromolecules*, we recently reported a set of perfectly regioregular pendant terfluorene functionalized polyolefins (general architecture D of Figure 1), where PLED current density was found to depend on the number of intermediary polymer backbone carbons separating the pendant groups (spacer length); this also had a profound impact on device external quantum efficiency.[24] This motivated us to initiate a space charge limited current (SCLC) charge-carrier mobility study on similar regioregular electroactive polyolefins for PLEDs. We present here a set of six polymers containing pendant 2,7-bis(phenyl-*m*-toluylamino)fluorene (TPF) groups where spacer lengths have been varied to control charge-carrier mobility. The TPF groups are placed on exactly every 9th, 15th, or 21st carbon along the polymer backbone. Furthermore, the impact of morphology in these materials was probed by saturating the polymer backbone alkene remnants of ADMET to produce materials with somewhat different ordering. With one exception, which is a special case due to difficulties in processing and purification, these polymers exhibit spacer length dependent SCLC charge-carrier mobilities ranging over 3 orders of magnitude. Similar to previous studies,[25] as the ratio of conjugated to nonconjugated material increases, mobility markedly increases.

2,7-Bis(phenyl-*m*-toluylamino)fluorene (TPF) was chosen as the hole transporter in this study because it is structurally identical to the commonly used hole transporting material 4,4′-Bis(phenyl-*m*-toluylamino)biphenyl (colloquially called triphenyldiamine, TPD), except that TPF contains an aryl ring bridging methylene unit that allows for easy decoration with polymerizable groups.[26] Furthermore, we anticipated the potentially poor solubility of our target polymers, thus the *m*-toluyl derivative of TPF was chosen, as opposed to the tetraphenyl alternative, because we expected the former variant would suffer solubility issues to a lesser extent. Our worries proved founded for polymer **PE9TPF**, as will be addressed below.

Scheme 1 shows the synthesis of six sequenced triarylamine functionalized polyolefins containing hole transporting groups on every 9th, 15th, or 21st carbon. The synthesis begins with the preparation of TPF via Buchwald coupling of 3-methyl-*N*-phenylaniline with 2,7-dibromofluorene, as first reported by Thompson and co-workers.[23] Due to the relative instability of TPF toward air oxidation at C9, we found it inconvenient to carry out rigorous purification at this stage; therefore, the crude product was quickly carried through alkylation to produce stable monomers **1**−**3**. However, prior to alkylation, we found it necessary to pass the crude TPF product through a short plug of silica using toluene as eluent to remove spent palladium catalyst; failure to do so results in isomerization of the terminal alkenes to internal alkenes. Purification of the monomers was achieved using silica gel chromatography with isolated yields over two steps of 51, 44, and 48% for **1**, **2**, and **3** respectively.

Because the monomers were either crystalline solids or highly viscous liquids, ADMET polymerizations required the use of a high boiling solvent and dynamic vacuum according to the procedure developed by Plenio and Weychardt.[27] After rigorous purification by passage through short plugs of silica gel, Soxhlet extraction, and multiple precipitations, the isolated polymers exhibited molecular weights and polydispersity indices typical for ADMET polymerization (see Table 1), although competing ring closing metathesis of **1** and its reduced solubility resulted in a somewhat lower molecular weight for **P33TPF**. The same issue, except for solubility, was encountered and discussed in greater detail in our recent report on terfluorenylidene functionalized polyolefins.[24,28] Finally, in an effort to enhance ordering in the materials by removal of the morphologically disruptive *cis* and *trans* backbone alkene remnants of ADMET polymerization, synthesis was completed with hydrogenation of the polymers to produce poly(ethylene-*co*-TPF) derivatives **PE9TPF**, **PE15TPF**, and **PE21TPF** and rigorous polymer purification was repeated. Upon hydrogenation of **P33TPF**, however, the resultant polymer (**PE9TPF**) became even less soluble, resulting in the need to run the hydrogenation reaction relatively dilute with a larger catalyst loading to affect dissolution and adequate reaction kinetics. Ultimately, the poor solubility of **PE9TPF** prevented it from being passed though silica for removal of spent catalyst residues; thus, methanol Soxhlet extraction alone was utilized for this purpose with unknown efficacy. It should be noted that all polymers were sufficiently pure to pass elemental analysis and the saturated polymers **PE*x*TPF** exhibited total disappearance of backbone alkene signals by NMR (see SI for experimental details).

As shown in Table 1, the polymers were fully amorphous with T_gs clearly dependent on the length of the flexible aliphatic spacers separating the relatively rigid aryl groups. Interestingly, while the same trend is present in analogously sequenced

Scheme 1. Synthesis of Hole Transporters

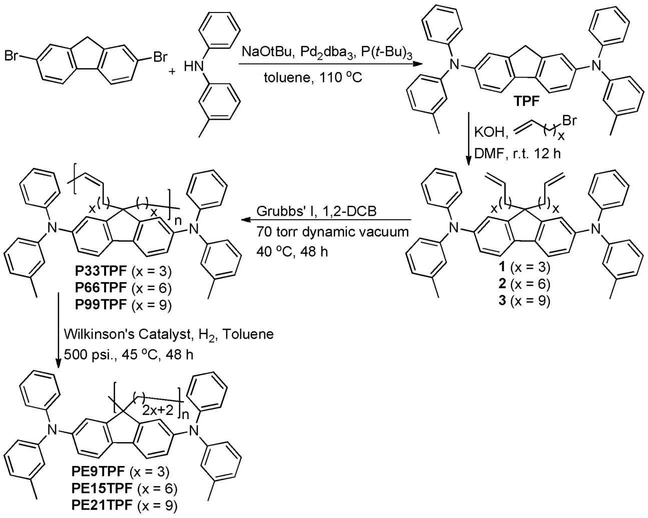

Table 1. Molecular Weight and Thermal Data

polymer ID	M_n (kDa)	PDI	T_g (°C)
P33TPF	14.4	1.71	82
PE9TPF	15.4	1.71	78
P66TPF	23.3	2.04	75
PE15TPF	24.9	2.01	68
P99TPF	30.1	1.84	57
PE21TPF	30.1	1.88	61

terfluoreneylidene functional polyolefins we previously reported,[24,28] it occurs at substantially higher temperatures here. T_gs in the former ranged from 29 to 50 °C. Because both sets of materials contain identical spacer lengths (i.e., chromophores on every 9th, 15th, or 21st carbon) and because the glass transition is expected to result from similar backbone chain motion in both sets, the fact that T_gs are higher in the aryl amines indicates tighter packing, leading to more restricted segmental motion. Both tight packing and high T_gs are advantageous from the viewpoint of optoelectronic device fabrication.

Having successfully isolated regioregular hole transporting polyolefins, we were motivated to investigate their hole mobilities. The SCLC method was chosen as it is representative of the current-density driving-voltage (*J*–*V*) characteristics of a PLED.[29] Details of the experimental procedures can be found in the Supporting Information; however, hole-only SCLC devices were fabricated with 70 nm thick polymer films spun cast from chlorobenzene using an architecture of substrate/ITO/PEDOT:PSS/polymer/Au. It is worth mentioning that we initially investigated molybdenum trioxide as a hole injection layer due to its reported efficacy for triaryl amine based materials;[30,31] however, the use of PEDOT:PSS as the hole injecting contact yielded devices that more closely fit the SCLC model. This result may actually be beneficial as PEDOT:PSS is a well established and easy solution processed hole transporting layer commonly used in PLEDs, while molybdenum trioxide, which only recently can be processed from solution,[32] is far more often deposited via an expensive and industrially undesirable thermal evaporation.

Figure 2 shows current density–voltage (*J*–*V*) data, which has been fit to the field-dependent SCLC equation (eq 1) for three representative devices fabricated from the unsaturated polymers **P*xx*TPF**, while Figure 3 shows the averaged zero field charge-carrier mobilities measured from eight devices for each polymer. Representative SCLC plots for the saturated polymers, **PE*x*TPF**, and current–voltage (*I*–*V*) plots for all polymers may be found in the SI.

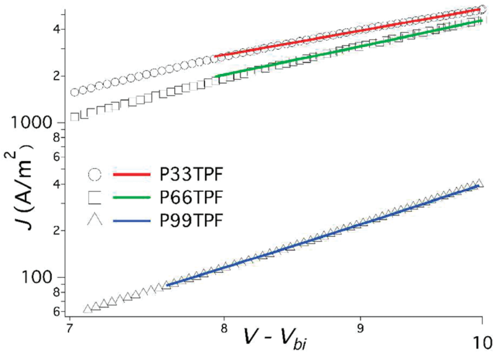

Figure 2. Field-dependent SCLC fits for three representative hole-only devices fabricated with the unsaturated polymers.

$$J = \frac{9}{8}\mu_0\varepsilon_r\varepsilon_0 \exp\left(0.891\gamma\sqrt{\frac{V}{L}}\right)\frac{V^2}{L^3} \tag{1}$$

Field-dependent SCLC equation, where *L* was measured by AFM (tapping mode) to be 70 nm and a value of 3 was used for ε_r (relative permittivity).

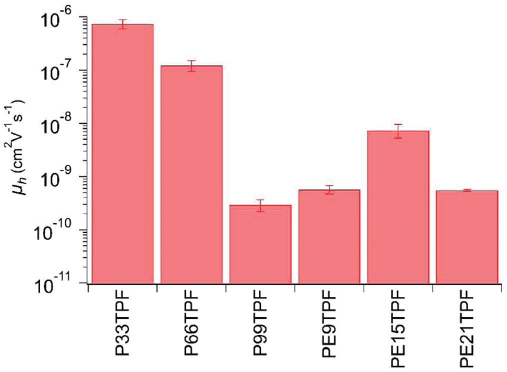

Figure 3. Average zero field SCLC hole mobilities (μ_h) from eight devices for each polymer. Error bars represent one standard deviation on the logarithmic scale.

Relatively large differences in the *J*–*V* characteristics of the devices and mobilities of the materials are readily visible and follow a logical trend. Except for **PE9TPF**, as the spacer length between pendant TPF groups increases, *J*s at constant *V* and charge-carrier mobilities both drop. This trend is expected because increasing the spacer length increases the intermolecular hopping distance for charge transport between pendant groups of the same chain, as well as the relative content of insulating polymer, thereby likely impeding charge hopping between electroactive units of different chains. However, **PE9TPF** does not fit the aforementioned trend. We believe this anomaly is due to the relative difficulty of processing the polymer and the possibility that it contains some residual catalyst residues due to the purification issues mentioned above. All other polymers were spun cast from 15 mg/mL chlorobenzene solutions at room temperature (stirred overnight). However, dissolution of **PE9TPF** required heating at 50 °C overnight and 100 °C prior to spin coating, which may have led to some polymer degradation and the formation of hole traps.

In summary, the zero field hole mobilities reported here, which range from 2.9×10^{-10} cm^2/(V s) to 7.4×10^{-7} cm^2/(V s) (averages), are lower than other high performance hole transporting materials; however, several exceed the zero field electron mobilities reported for common electron transporting materials/emitters.[33] For example, the zero field electron mobility of the very well-known emitter/transporter Alq_3 is 4.7×10^{-9} cm^2/(V s).[33] By varying the spacer length separating pendant hole transporting chromophores, we have demonstrated control of mobility over 3 orders of magnitude, encompassing the electron mobilities of common electron transporters and emitters, and thus, have made it feasible to fabricate electroactive polyolefin-based PLEDs with well-balanced charge-carrier mobilities and potentially improved performance. Furthermore, we believe this approach to mobility control could be applied to other hole transporting chromophores with energy levels matched to various emitters. In addition, the range of mobilities could be extended to both higher and lower values simply by decreasing or increasing the spacer lengths beyond those reported here via known synthetic protocols.[34,35]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, NMR data, mass spectrometry data, elemental analysis, representative SCLC charge-carrier mobility plots with eight-device averaged μ_h shown in accompanying text boxes, and current−voltage plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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