Perfectly Regioregular Electroactive Polyolefins: Impact of Inter-Chromophore Distance on PLED EQE

Brian S. Aitken, Patrick M. Wieruszewski, Kenneth R. Graham, John R. Reynolds,* and Kenneth B. Wagener*

The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611-7200, United States





ABSTRACT: Acyclic diene metathesis polymerization (ADMET) was used to synthesize a series of perfectly regioregular polyolefins, in which the number of backbone atoms between pendant terfluorene groups was precisely controlled at 8, 14, or 20 carbons. Analogous random copolymers containing identical chromophore densities were also synthesized to study the impact of regioregularity on the performance of this class of materials in polymer light emitting diodes (PLEDs). Additionally, the backbone alkene remnants of ADMET were saturated to generate materials with somewhat different ordering. These saturated derivatives led to improvements in PLED external quantum efficiencies (EQEs) over their unsaturated analogues in most cases, with a large improvement in one material. Charge mobility, as manifested in current density during PLED characterization, and relative solid-state fluorescence quantum yield (Φ_F) also exhibit reasonable dependencies, with longer distances between electroactive groups yielding lower PLED current densities and higher Φ_F . Regioregularity has the opposite effect, giving rise to higher current densities and lower Φ_F as compared to regiorandom analogues.

INTRODUCTION

As global economic development occurs, the demand for cheap, energy-efficient displays and lighting continues to increase,^{1–3} placing higher demands on our understanding of design parameters for fabrication of high performance polymer light emitting diodes (PLEDs). These devices can be processed from solution by, for example, ink jet printing or spin coating, as opposed to the costly processes requiring high temperature, ultra clean conditions and high vacuum needed in inorganic LED and small molecule OLED construction. Thus, PLEDs afford a low cost option for the fabrication of large and or flexible displays such as television screens, computer monitors, and large emissive lighting surfaces.^{4–10}

However, even state-of-the-art PLEDs currently suffer from lower performance compared to their inorganic and molecular counterparts.^{3,9–24} Figure 1 shows that the design of efficient PLEDs necessitates a balance of hole and electron mobilities, which must also be sufficiently high, to ensure that charge recombination occurs near the center of the emissive layer of the device.^{22,25–31} For those based on emission from singlet excitons, high fluorescence quantum yields ($\Phi_{\rm F}$) are required as well. However, attaining high performance in both parameters for one material is quite challenging. Highly ordered organic semiconductors tend to exhibit increased charge mobility over their amorphous counterparts, $^{27,32-38}$ but ordering may simultaneously reduce $\Phi_{\rm F}$ by enhancing quenching mechanisms via increased energy migration and formation of non emissive complexes. $^{39-47}$

Donor-donor energy migration (DDEM, also referred to as homo resonance energy transfer), a process closely related to Förster resonance energy transfer (FRET) but between chemically identical species,⁴⁸⁻⁵⁷ enhances quenching in fluorescent materials by allowing excited state energy to migrate via adjacent identical fluorophores to either dark complexes (static quenching) or to fluorophores which have a greater propensity to undergo dynamic quenching as a result of

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Figure 1. Schematic of the various processes leading to quenching or light emission that may occur in a PLED.

their microenvironments; 58-62 the latter is referred to as partial donor-donor energy migration (PDDEM).⁶³⁻⁶⁸ The rate of resonance energy transfer (RET) is dependent on, among other variables, the distance between energy donor and energy acceptor to the inverse sixth power.^{66,69,70} Therefore, increasing the intermolecular distance between the fluorophores of interest is advantageous if one wishes to reduce the effects of RET. Particularly, in PLEDs and OLEDs, unintentional RET is disadvantageous as it reduces the device's external quantum efficiency (EQE) by enhancing the effects of both selfquenching and quenching due to impurities such as residual transition metal catalysts. However, the immediate solution of increasing the distance between chromophores may be deleterious to device performance, since charge mobility will simultaneously drop. The obvious question is "how distant should chromophores be to limit quenching while, still allowing for sufficiently high charge mobility for exciton generation?" One might attempt to approach the problem theoretically, however calculation of the resulting changes in DDEM, PDDEM, and FRET rates upon variation of the aforementioned distance, and ultimately the corresponding changes in $\Phi_{\rm F}$, requires knowledge of the geometric attitude of the donor with respect to the acceptor for calculation of the orientational factor (κ^2) in the Förster treatment. 55–57,66–71 This parameter is extremely difficult or even impossible to predict for materials of the general type presented here, particularly in the solid state, where orientational randomization is quite slow and precludes the oft used approximation of $\kappa^2 = 2/3$, which is valid for small molecules in solution.^{55–57,66–68,70,71} Furthermore, estimation of the variation in charge mobility, which will invariably result from such structural changes, is impossible at

the current level of theory, and charge injection rates remain an additional theoretical problem.⁷² Therefore, an empirical structure–property study to assess the impact of chromo-phore–chromophore distance variation on PLED performance is necessary.

To determine the effects of chromophore separation on device parameters, we have prepared a set of perfectly regioregular electroactive polyolefins with carefully controlled average chromophore-chromophore distances. As shown in Figure 2A, regioregular electroactive polyolefins comprise a



Figure 2. Architecture of polymeric electroptic materials.



Scheme 1. Synthetic Approach to Regioregular Electroactive Polyolefins and Two Regiorandom Analogues

class of materials in which the active pendant group occurs at exactly defined backbone run length intervals (spacer lengths).^{73,74} These regioregular materials are analogous to previously reported vinyl type or regiorandom polymers containing pendant electroactive moieties (Figure 2B).^{75–93} Similar to main chain π -functional materials (Figure 2C),^{94–98} pendant π -functional polymers offer the opportunity for inclusion of various electroactive units, which may serve their purposes cooperatively (e.g., various chromophores for white emission, emissive units and charge transporters, etc.)^{84,92,93} and thus afford an interesting and relatively new avenue for exploration into optoelectronic materials, as compared to conjugated polymers (Figure 2D).

Good control over the average distance between chromophores can be accomplished via acyclic diene metathesis polymerization (ADMET) of symmetric α, ω -diene functionalized chromophores followed by alkene hydrogenation or, as was demonstrated in our earlier work, by post polymerization coupling of chromophore fragments to regioregular borylated polyolefins.^{73,74} In the work reported here, terfluorenylidenes were placed pendant to fully linear polyethylene at exactly defined spacer lengths via the former method. We have found that polymers with longer spacer lengths exhibit higher PLED performance, despite yielding reduced current densities at identical device driving voltages. Furthermore, analogous regiorandom polymers exhibit enhanced relative solid-state $\Phi_{\rm F}$, presumably due to relatively reduced ordering and therefore less quenching. However, they also exhibit somewhat lower charge mobilities, as manifested in reduced PLED current densities, also resulting from their disorder. The concepts demonstrated here may also prove useful in the design of polymers for other Φ_F dependent devices such as scintillation detectors^{99–101} and luminescent solar concentrators.^{102–106}

EXPERIMENTAL SECTION

Materials and Instrumentation. All materials were purchased from Aldrich and used as received, unless noted otherwise. Absorption spectra were measured with a PerkinElmer Lambda 25 UV–vis spectrometer. Photoluminescence spectra were obtained using a Horiba Jobin Yvon Fluorolog-3 fluorimeter.

Synthesis. Synthesis of these materials was briefly described elsewhere;⁷³ however, due to length constraints, characterization was

limited to differential scanning calorimetry and gel permeation chromatography of the polymers. Complete characterization of all materials, including NMR, mass spectrometric data, and elemental analysis is now fully divulged in the Supporting Information for this article.

Device Fabrication and Characterization. PLEDs were fabricated with a device architecture of glass/ITO/PEDOT:PSS/ polymer/LiF/Al. Prepatterned indium tin oxide (ITO) coated glass (25 mm ×25 mm) was used with either a 12 or 20 Ω/\Box resistance. ITO-coated glass was cleaned by sequential sonication in sodium dodecyl sulfate solution, 18.2 M Ω MiliQ water, acetone, and 2propanol. Immediately following 2-propanol sonication, substrates were blown dry with nitrogen and exposed to oxygen plasma for 20 min. Under a particle free hood, substrates were spun cast with PEDOT:PSS (Baytron P VP Al 4083 which was filtered through 0.45 μ m nylon filters) at 5000 rpm for 45 s, then annealed for 20 min at 130 °C in an Ar filled glovebox with H₂O and O₂ concentrations of less than 0.1 ppm. In the glovebox, active layer solutions were prepared at 15 mg/mL concentrations in anhydrous and deoxygenated chlorobenzene and spun cast onto the PEDOT:PSS coated substrates for 60 s at 1000 rpm. Cathodes consisting of 1 nm LiF and 100 nm Al were thermally deposited on the substrates at a pressure of 1×10^{-6} mbar through shadowmasks defining 8 pixels/substrate, each with an area of 0.071 cm². Electroluminescence spectra were collected using an ISA SPEX Triax 180 spectrograph, maintained at ~140 K, with a Keithley 2400 sourcemeter driving the device at a constant current. Radiant emittance and current density data were acquired using a custom written LabVIEW program coupled with a calibrated UDT Instruments silicon diode and a Keithley 2400 sourcemeter. Luminance data were collected using a Konica CS-100 minolta chromameter with the device at a constant voltage bias.

RESULTS AND DISCUSSION

Synthesis and Physical Characterization. Perfectly regioregular polymers of the general architecture shown in Figure 2A may be synthesized in at least one of two ways. In our first report, we described a general method which allows for Suzuki coupling of aryl groups to regioregular borylated fluorene functionalized polyolefins.⁷⁴ However, this method was limited to polymers with no more than one electroactive group on every 21st polymer backbone carbon. This limitation was the result of solubility issues stemming from ionization of the polymer during the Suzuki coupling step. As shown in Scheme 1, this problem has been alleviated by reversing the

order of synthesis from post polymerization modification for installation of the chromophore to polymerization of fully functionalized monomers. The latter method allows for increased chromophore density, and materials containing chromophores on exactly every 21st, 15th, and ninth carbon have been prepared (though presumably, these numbers could be raised or lowered further via known synthetic protocols^{107–109}). Furthermore, the choice of terfluorenylidenes as the active species allows for hydrogenation of the residual backbone olefin after ADMET, thus providing a handle on material morphology, which is known to dramatically change upon olefin hydrogenation in similar polymers.¹¹⁰ The regioregularity of these polymers, as opposed to the regiorandom materials produced in various copolymerizations, and the distribution of chromophore densities over a reasonable range, provides good control over the average distance between electroactive groups in a set of materials. Their interchromophore distances as well as any potential aggregates' sizes and shapes should exhibit greater homogeneity (reduced polydispersity in distance/size/shape) than in analogous random copolymers, as previously observed in other systems containing interactive pendant groups.^{111,112} Although the synthesis of the polymers in this work was reported previously,⁷³ the design rationale and issues encountered during their preparation were not provided in detail, thus a more thorough discussion can be found in the Supporting Information.

Characterization of the polymers by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), polarized optical microscopy, and atomic force microscopy (AFM) was carried out. The GPC and DSC data, were reported previously⁷³ and can also be found in the Supporting Information. Molecular weights were high in all cases ($M_n = 21-65$ kDa), although P-3,3-TF (21 kDa) and P-3,3-TF-S (22 kDa) exhibited somewhat lower M_n and PDI due to a cyclization issue also discussed in the Supporting Information. No melting transitions were detected during DSC experiments up to 200 °C at various scan rates ranging from 1 to 20 °C/min, and no birefringence was observed under polarized light microscopy. To further probe morphology, AFM measurements were carried out on spun cast polymer films; however, we again observed no unique features in any polymer. Instead, AFM indicated only very flat surfaces with root mean squared surface roughnesses around 0.3 nm (see Supporting Information for micrographs).

UV–Vis Characterization. To assess whether or not control over Φ_F in this system was achieved, thin films with nearly identical optical densities (±5%) were prepared by spin coating onto glass substrates from dilute solutions of each polymer in chloroform. Using identical instrument parameters, the front face fluorescence spectra of each film was then measured and corrected for the small changes in optical density of each sample (see Figure 3). Each measurement was carried out in duplicate after rotating the substrate 90°, and two films were prepared for each polymer (total of four measurements each).

Except for P-9,9-TF-S, it is evident that the relative $\Phi_{\rm F}$ increases as the spacer between each fluorophore increases in length, and that regiorandom analogues also exhibit increased $\Phi_{\rm F}$. Both increases in $\Phi_{\rm F}$ are presumably due to reduced $\pi - \pi$ interaction, which is known to systematically vary as a function of copolymer composition in regiorandom pendant π -functional materials;^{87–90} reduced $\pi - \pi$ interactions lead to



Figure 3. Solid-state absorbance and front-face fluorescence spectra (corrected for optical density at excitation = 350 nm). Error bars are 95% confidence intervals for the corrected fluorescence intensity at λ_{max} . All data points used to create the plots were averaged over four trials.

decreased energy migration and quenching. Furthermore, as evidence against the possibility of method error or false results due to various levels of residual transition metal catalyst contamination, we carried out similar comparative fluorescence measurements in chloroform solution; all polymers exhibited identical fluorescence intensities and therefore identical Φ_F (see Figure 4).



Figure 4. Chloroform solution absorbance and fluorescence spectra (corrected for optical density at excitation =350 nm) for all polymers.

Careful examination of the data will show that P-9,9-TF-S is the only polymer which does not fit the aforementioned spacer length trend; indeed, it has the lowest $\Phi_{\rm F}$ of the backbone-saturated polymers. This is perhaps the result of a unique morphology relative to the other materials. However, as previously discussed, we have been unable to directly observe any morphological features by AFM or optical microscopy in any of these materials.

PLED Fabrication and Characterization. Having demonstrated systematic control of solid-state Φ_F through polymer backbone run length variation, we were motivated to prepare relatively simple PLEDs using a Glass/ITO/PEDOT:PSS/

ActiveLayer/LiF/Al architecture. Electroluminescence spectra, radiant emittance, current density, and luminance data were collected for each device, and EQEs were calculated.

As shown in Figure 5, all devices exhibited similar but subtly different electroluminescence spectra. This is to be expected



Figure 5. Normalized electroluminescent spectra of saturated polymers.

since each polymer contains identical chromophores but differing degrees of interaction between them. On the other hand, device performance varies greatly. Figures 6 and 7 show



Figure 6. Luminance and current density vs driving voltage for devices fabricated from unsaturated polymers.

the current density and luminance as a function of applied voltage for devices fabricated from unsaturated and saturated polymers, respectively. These data are from single devices; however, device reproducibility is excellent as indicated by averaged EQE data shown in Figure 8. Examination of the current density plots for each device reveals an interesting trend; as the polymer backbone run length separating pendant chromophores increases, current density at identical driving voltages decreases. This is presumably due to reduced charge mobilities resulting from lower chromophore densities and longer hopping distances. Furthermore, regiorandom P-R21-TF, which is an analogue of P-9,9-TF, exhibits a somewhat



Figure 7. Luminance and current density vs driving voltage for devices fabricated from saturated polymers.



Figure 8. Average EQEs measured from eight pixels per polymer (error bars represent a full standard deviation).

lower current density. One might attribute this difference to reduced charge mobility resulting from reduced ordering in the regiorandom polymer; however, P-R21-TF-S and P-9,9-TF-S devices show nearly identical current densities, although the latter is somewhat special in its characteristics, as will be discussed below.

In contrast with the current density and solid-state $\Phi_{\rm F}$ data, which shows general spacer length effects, device luminance output is somewhat less systematic. Instead, P-3,3-TF, P-3,3-TF-S, P-6,6-TF, and P-6,6-TF-S show similar luminance (<35 cd/m²), P-R21-TF and P-R21-TF-S show some improvement (max of 43, 45 cd/m² respectively), while P-9,9-TF and P-9,9-TF-S show far greater luminosity (max of 93, 366 cd/m² respectively). Finally, EQEs have been calculated and are shown in Figure 8. Again, a general trend emerges, with longer backbone run lengths resulting in improved EQEs, thus it can be concluded that lower chromophore densities are actually beneficial to the efficiency of this class of materials in PLEDs. Additionally, for all polymers except P-9,9-TF-S, device EQE was only slightly effected by backbone saturation; however in P-9,9-TF-S, saturation led to an over 2-fold improvement in EQE. Much like the fluorescence and PLED luminance measure-

ments, in which P-9,9-TF-S was an outlier, such an improvement indicates again that morphological changes may have occurred as a result of backbone saturation in this polymer and that such changes play an important role in its performance. Furthermore, electrode surface texturization, which will be discussed below, provides additional evidence for morphological differences between the materials studied here.

Having demonstrated systematic control of PLED EQE via spacer length variation, it is important to discuss two anomalous observations: emergence of gold coloration on the aluminum electrode surface of *only* P-9,9-TF-S devices, indicative of morphological changes leading to surface texturization, as well as temporal and spatial modulation of PLED pixel luminosity. As expected, vacuum-deposited aluminum electrodes for all other devices were bright silver in color (see Figure 9). Here again, the morphological differences



Figure 9. Optical microscope images of electrode surfaces on P-9,9-TF-S and, as a representative image, P-3,3-TF-S devices.

in P-9,9-TF-S are highlighted by the occurrence of electrode surface coloration/texturization; however, attempts to elucidate the nature of this phenomenon via AFM of the electrode have proven quite challenging.

The observation of spatial and temporal fluctuation of PLED luminosity (see Figure 10) is somewhat less puzzling. Since the



Figure 10. Sequence of time lapsed photographs of P-9,9-TF-S pixel at a constant driving voltage of 13 V beginning at device turn on (top left) and ending 22.5 s later (bottom right).

 $T_{\rm g}$ s of these materials are relatively low (22–50 °C, see Supporting Information), we believe the fluctuation results from Joule heating, which has been demonstrated to raise the temperature of PLEDs by several tens of degrees,^{113–115} thus providing the polymer chains with sufficient thermal energy to undergo long-range segmental motion. This would allow microdomains to temporarily attain a highly emissive morphology before temporarily changing to a darker one. Furthermore, overall luminance increases over the first few seconds of device operation before reaching a plateau, indicating that Joule heating is, in this case, beneficial to device performance. The luminosity fluctuation continues until the device is turned off or is driven to burn out at high voltage biases. Annealing at 80 °C (well above polymer $T_{\rm g}s$) before carrying out measurements makes no difference in EQE or the occurrence of the luminosity fluctuation. We are currently investigating the possibility of utilizing the residual backbone alkenes in the unsaturated polymers for cross-linking, as this would reduce the segmental motion hypothesized as the cause of this optical phenomenon.

CONCLUSIONS

We have synthesized and characterized a series of six perfectly regioregular electroactive polyolefins and two regiorandom analogues. Differential scanning calorimetry and polarized optical microscopy illustrate that these materials are amorphous. They exhibit spacer length dependent solid-state $\Phi_{\rm F}$, PLED current densities (presumably resulting from spacer length dependent charge mobilities), and PLED EQEs. In summary, longer spacer lengths result in higher $\Phi_{\rm E}$, lower charge mobility (as manifested in PLED current density), and higher PLED EQE. Furthermore, by comparing the four P-9,9 and P-R21 derivatives, we found that regioregularity reduces solid-state $\Phi_{\rm F}$. Interpretation of current densities in the set of four is less straightforward; charge mobility was improved by regioregularity in the unsaturated pair but not in the saturated pair (which we believe is a special case due to suspected morphological differences in P-9,9-TF-S). While the PLED performance of this series of polymers leaves much to be desired, we believe the general trends which they exhibit will be useful in the design of new electroactive materials based on pendant π -functional architectures, and their direct application in other $\Phi_{\rm F}$ dependent devices such as scintillation detectors or luminescent solar concentrators may prove more valuable.

ASSOCIATED CONTENT

S Supporting Information

Synthesis discussion, detailed experimental data, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: (J.R.R.) Reynolds@chem.ufl.edu; (K.B.W.) Wagener@chem.ufl.edu.

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