

Effects of Intercalation on the Hole Mobility of Amorphous Semiconducting Polymer Blends

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Fullerenes have been shown to intercalate between the side chains of many crystalline and semicrystalline polymers and to affect the properties of polymer:fullerene bulk heterojunction solar cells. Here we present the first in-depth study of intercalation in an amorphous polymer. We study blends of the widely studied amorphous polymer poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (MDMO-PPV) with a variety of molecules using photoluminescence measurements, scanning electron microscopy, and space-charge limited current mobility measurements. The blends with elevated hole mobilities exhibit complete photoluminescence quenching and show no phase separation in a scanning electron microscope. We conclude that intercalation occurs in MDMO-PPV:fullerene blends and is responsible for the increase in the MDMO-PPV hole mobility by several orders of magnitude when it is blended with fullerenes, despite the dilution of the hole-conducting polymer with an electron acceptor.

Introduction

Polymer:fullerene bulk heterojunction solar cells, with NREL-certified power conversion efficiencies as high as 7.9%, offer promise as a low-cost alternative to silicon solar cells.^{1–8} The molecular mixing and morphology of the polymer (electron donor) and fullerene derivative (electron acceptor) in these bulk heterojunction solar cells heavily influence cell performance by affecting important processes such as exciton splitting, charge transport, and

recombination.^{9–15} X-ray diffraction has been used to demonstrate the formation of a molecularly mixed phase in which fullerene derivatives intercalate between the polymer side chains in many crystalline and semicrystalline polymer:fullerene blends.^{16,17} Intercalation also likely occurs in amorphous polymers, but detection by X-ray diffraction is challenging because one cannot simply measure the increase in lattice spacing that is observed when intercalation occurs in crystalline polymers.

In this paper, we show that fullerenes intercalate between the side chains of the widely studied amorphous polymer poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (MDMO-PPV). Prior to performing the experiments shown here, there were several reasons to suspect that intercalation occurs. First, MDMO-PPV has sufficient space between the side chains to accommodate a fullerene, so it is possible for fullerenes to intercalate (Figure 1a).¹⁶ Like other intercalated systems,^{16,17} MDMO-PPV:phenyl-C61-butyric acid methyl ester (PC₆₁-BM) solar cells have their highest efficiencies at a 1:4 polymer:fullerene weight ratio.⁶ Nonintercalated blends have optimal efficiencies near a 1:1 polymer:fullerene ratio, because it is best to have approximately equal volumes of the electron-conducting (pure fullerene) and hole-conducting (pure polymer) phases to allow both electrons and holes to be extracted.^{16,17} In intercalated blends, on the other hand, no pure fullerene phase forms until fullerenes

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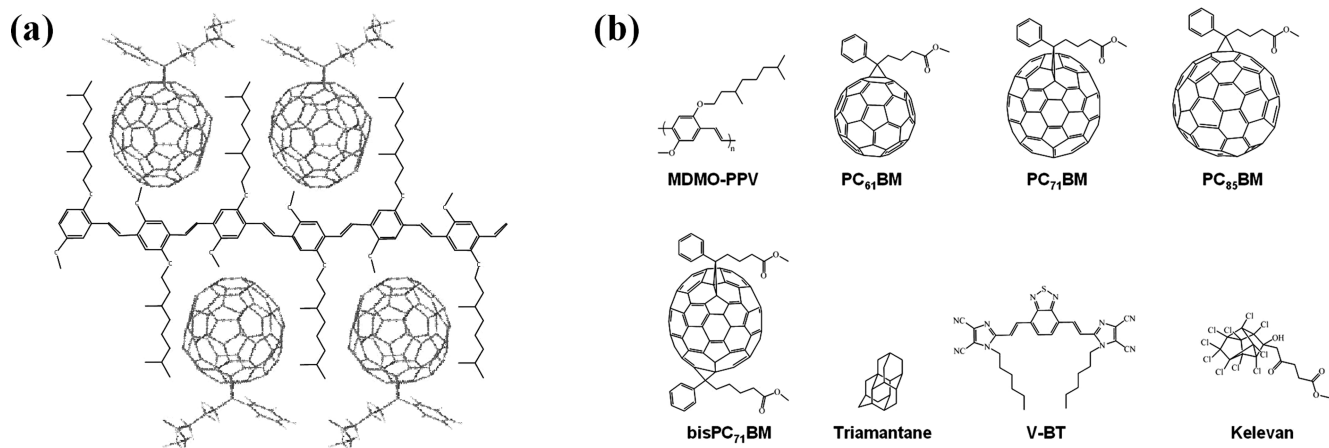


Figure 1. (a) Illustration of how PC₆₁BM might intercalate in MDMO-PPV in a planar conformation. Because MDMO-PPV is an amorphous polymer, the actual structure of intercalated MDMO-PPV:PC₆₁BM is likely not planar as shown above. (b) Structures of MDMO-PPV and the molecules used.

have intercalated between all available spaces between the polymer side chains. Intercalated blends therefore optimize at higher fullerene concentrations, usually near 1:4 polymer:fullerene, the optimal blend ratio for MDMO-PPV:PC₆₁BM solar cells. In addition, atomic force microscopy (AFM) and transmission electron microscopy (TEM) have been used to show that MDMO-PPV and PC₆₁BM mix on the molecular level and no pure PC₆₁BM phase forms at concentrations below ~67 wt % PC₆₁BM.^{18–20} Assuming a monomer:fullerene ratio for the pure intercalated phase between 2:1 and 1:1, standard monomer:fullerene ratios for intercalated phases, the predicted concentration at which intercalation should be complete is between 63 and 78 wt % PC₆₁BM (Supporting Information).¹⁶ Thus, the onset of PC₆₁BM formation at ~67 wt % PC₆₁BM, which lies within this range, likely results from the completion of an intercalated MDMO-PPV:PC₆₁BM phase.

MDMO-PPV also exhibits the peculiar phenomenon that its hole mobility increases by several orders of magnitude when it is mixed with PC₆₁BM, despite the dilution of the hole-conducting polymer with an electron acceptor.^{19,21–24} Although this mobility increase has been observed using a variety of techniques that probe the mobility out of the plane of the substrate, field-effect transistor (FET) measurements, which probe in-plane mobility near

the substrate, have conflicting results with some reports of increased mobility upon PC₆₁BM loading²⁵ and some reports of no mobility increase.²⁶ Nevertheless, measurements of the out-of-plane mobility, the mobility relevant to solar cells, agree that the MDMO-PPV hole mobility increases upon blending with PC₆₁BM. If the hole mobility of MDMO-PPV did not increase when blended with PC₆₁BM, MDMO-PPV:PC₆₁BM cells would suffer from space-charge limited current and unbalanced charge transport, since the hole mobility of pure MDMO-PPV (5×10^{-7} cm²/(V s)) is several orders of magnitude less than the electron mobility of PC₆₁BM (2×10^{-3} cm²/(V s)).^{21,27} The increase in the MDMO-PPV hole mobility therefore reduces space-charge limited current and enables MDMO-PPV:fullerene solar cells to achieve efficiencies around 3%.^{28,29} Several theories have been proposed to explain the increase in mobility. Some have suggested that the PC₆₁BM, which usually transports electrons, might also transport holes in these blends.^{23,30} This scenario seems unlikely because holes would have to overcome a 1 eV energy barrier in order to move from the MDMO-PPV highest occupied molecular orbital (HOMO) (5.1 eV) to the PC₆₁BM HOMO (6.1 eV). Another theory is that PC₆₁BM interacts with the MDMO-PPV polymer chains, which coil into ring-like structures in pure MDMO-PPV,^{31,32} causing the chains to uncoil and consequently improving intermolecular interactions.^{21,23,33} However, no one has given a detailed description of this mechanism.

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We propose that PC₆₁BM intercalation between the MDMO-PPV side chains, shown schematically for a planar conformation in Figure 1a, inhibits the coiling of the polymer chains and therefore increases the conjugation length, intermolecular interactions, and hole mobility.¹⁶ In contrast, PPVs with symmetric side chains, which do not have enough space between the side chains for fullerenes to intercalate, show considerable phase separation at a 1:1 polymer:fullerene ratio and do not exhibit a significant increase in mobility upon blending with fullerenes.^{6,22} Pure symmetric PPVs also have mobilities that are one to two orders of magnitude higher than the mobility of pure MDMO-PPV,^{6,22,31} most likely because the symmetric PPV chains do not coil.^{31,32} Intercalation in MDMO-PPV:PC₆₁BM is supported by the fact that the hole mobility of these blends saturates above ~67 wt % PC₆₁BM,¹⁹ the same concentration at which a pure PC₆₁BM phase forms and within the predicted concentration range for the completed intercalated phase.^{16,18,20}

Experimental Section

Materials. MDMO-PPV ($M_n \approx 23\,000$), PC₈₅BM, and Kelevan were purchased from Aldrich. PC₆₁BM and PC₇₁BM were purchased from NanoC, and bisPC₇₁BM was purchased from Solenne BV. Triamantane was isolated from petroleum as described in reference 34. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was purchased from Baytron, and indium–tin oxide (ITO)-coated glass substrates were purchased from Sorizon. V-BT was synthesized as described in reference 35.

SCLC Mobility Measurements. Films for SCLC mobility measurements were prepared from chlorobenzene solutions. The films were spin-cast on PEDOT:PSS-covered ITO-coated glass substrates and vacuum-dried. The top electrodes were prepared by evaporating 100 nm of gold onto the films. The annealed samples were placed directly on a hot plate at 130 °C for 1 h. The current–voltage measurements were taken in the dark, and the SCLC mobility was extracted by fitting these curves with the SCLC equation. The film thicknesses used in the SCLC fits were measured using a Dektak profilometer. Several film thicknesses between 80 and 200 nm were examined for most blends. The film preparation, annealing, and current–voltage measurements were performed in a glovebox with a dry nitrogen atmosphere.

PL Measurements. PL measurements were performed in a dry nitrogen atmosphere by exciting films on glass substrates with an argon laser at a wavelength of 488 nm. The PL intensities were normalized by the absorbance of the films at 488 nm taken from measured UV–vis spectra.

SEM. The SEM images were obtained using a FEI XL30 Sirion SEM with a beam voltage of 5 kV. Films were spin-cast on conductive ITO-coated glass substrates to prevent charging.

Results and Discussion

To investigate intercalation in MDMO-PPV blends, we use photoluminescence (PL) measurements and scanning electron microscopy (SEM) images of several MDMO-PPV:molecule blends to determine which blends exhibit

phase separation in the polymer-rich region. We then perform space-charge limited current (SCLC) mobility measurements to determine which blends have elevated mobilities. For these experiments, MDMO-PPV is blended with several fullerenes (PC₆₁BM, PC₇₁BM,²⁹ PC₈₅BM,³⁶ and bisPC₇₁BM³⁷) as well as triamantane,³⁶ Kelevan, and a Vinazene derivative, V-BT³⁵ (Figure 1b).

Photoluminescence measurements were performed to determine how well the polymer and molecules mix in the blends. PL occurs when excitons recombine emissively prior to splitting at a donor–acceptor interface. Excitons originating on a polymer chain in an intercalated blend form within a few angstroms of a donor–acceptor interface. Consequently, these excitons are almost always disassociated by electron transfer before light emission can occur. In nonintercalated blends, excitons may have to travel through pure polymer domains to reach a donor–acceptor interface. As a result, some PL is expected in blends without intercalation. Complete PL quenching has been observed for several intercalated blends, whereas PL quenching in blends without intercalation is incomplete.^{16,17} The PL measurements, shown in Figure 2, indicate that nearly complete PL quenching is observed in MDMO-PPV blends with PC₆₁BM, PC₇₁BM, PC₈₅BM, and bisPC₇₁BM. MDMO-PPV blends with V-BT, on the other hand, exhibit only 96% PL quenching. The PL of MDMO-PPV blends with triamantane and Kelevan, which are not efficient electron acceptors and therefore would not show complete PL quenching even if they did intercalate, are shown in the Supporting Information.

To further investigate the mixing of MDMO-PPV with the molecules, we used SEM to look for phase separation in 1:1 (Figure 3a–g) and 4:1 (Supporting Information) MDMO-PPV:molecule blends. These blend ratios were examined because a pure phase of the added molecules should not form at polymer-rich ratios if intercalation occurs in these blends.^{16,17} On the other hand, if intercalation does not occur, the added molecules should form a second phase at both 1:1 and 4:1 MDMO-PPV:molecule ratios. No phase separation is observed for MDMO-PPV blends with PC₆₁BM, PC₇₁BM, PC₈₅BM, and bisPC₇₁BM. This result indicates that there might be molecular mixing in these blends, although the phase separation could be smaller than the nanometer-scale resolution of the SEM. Others have demonstrated molecular mixing in polymer-rich MDMO-PPV blends with PC₆₁BM^{18–20} and PC₇₁BM²⁹ using a variety of techniques. Phase separation was observed for MDMO-PPV blends with triamantane, Kelevan, and V-BT.

The PL measurements and SEM images indicate that intercalation does not occur in MDMO-PPV blends with triamantane, Kelevan, and V-BT, because these blends exhibit phase separation at 1:1 and 4:1 MDMO-PPV:molecule ratios. If intercalation had occurred in these blends, the added molecules should not have phase

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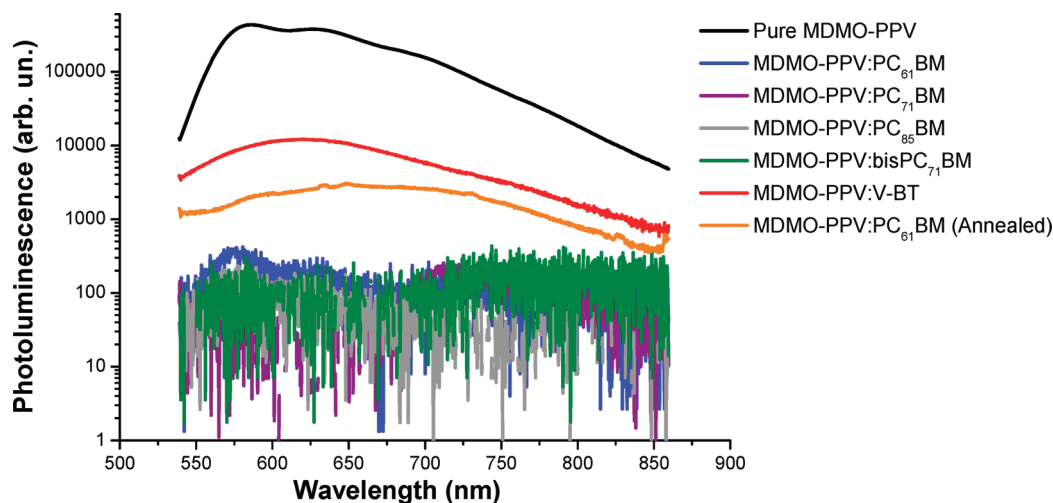


Figure 2. PL per photon absorbed for pure MDMO-PPV (black) and 1:4 MDMO-PPV:molecule blends with PC₆₁BM (blue), PC₇₁BM (purple), PC₈₅BM (gray), bisPC₇₁BM (green), and V-BT (red). The PL of 1:4 MDMO-PPV:PC₆₁BM annealed at 130 °C for 1 h is also shown (orange).

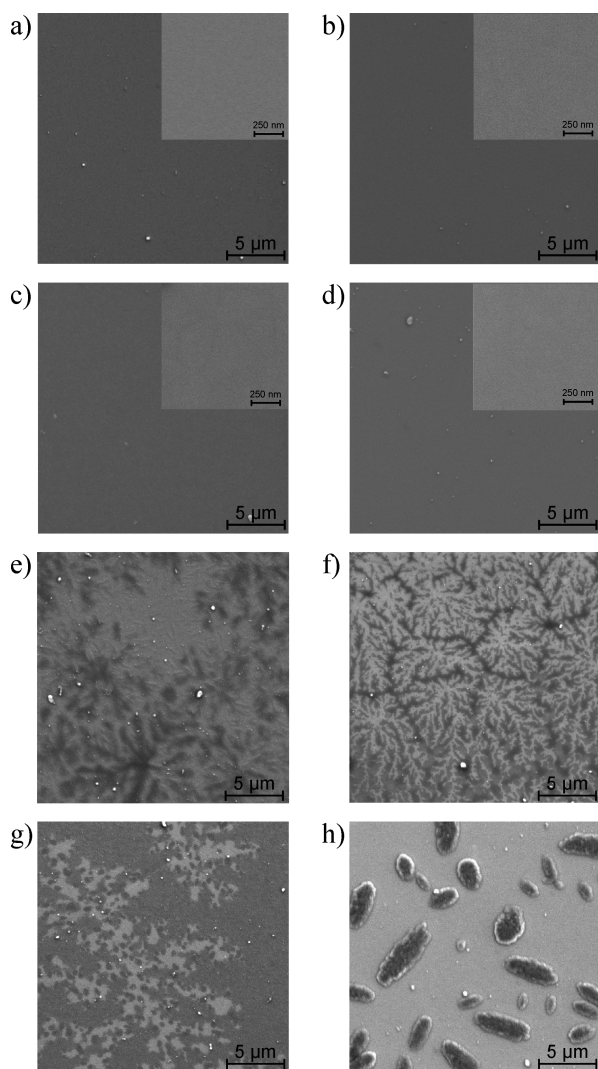


Figure 3. SEM images of 1:1 MDMO-PPV:molecule blends. The molecules in the blends are (a) PC₆₁BM, (b) PC₇₁BM, (c) PC₈₄BM, (d) bisPC₇₁BM, (e) triamantane, (f) Kelevan, and (g) VB-T. (h) 1:1 MDMO-PPV:PC₆₁BM blend annealed at 130 °C for 1 h.

separated from the polymer until they had filled all the spaces between the polymer side chains. On the other

hand, PC₆₁BM, PC₇₁BM, PC₈₅BM, and bisPC₇₁BM must intercalate in MDMO-PPV, because these molecules exhibit complete PL quenching and no phase separation observable in the SEM at 1:1 and 4:1 MDMO-PPV:molecule ratios.

Figure 4 summarizes the results of SCLC mobility measurements of several MDMO-PPV:molecule blends. The hole mobilities of MDMO-PPV blends with PC₆₁BM, PC₇₁BM, PC₈₅BM, and bisPC₇₁BM are several orders of magnitude higher than the hole mobility of pure MDMO-PPV. A significant hole mobility increase was not observed in MDMO-PPV blends with triamantane, Kelevan, or V-BT. Because the blends that do not exhibit phase separation in the polymer-rich region are the same blends that exhibit elevated hole mobilities, the hole mobility increase appears to be related to the formation of a molecularly mixed phase, which likely involves intercalation. It is interesting that bisPC₇₁BM appears to intercalate in MDMO-PPV even though it does not intercalate in poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene (pBTTT), a polymer that exhibits intercalation when mixed with PC₇₁BM.^{16,17} BisPC₇₁BM may intercalate in MDMO-PPV, because MDMO-PPV is amorphous and may therefore have more flexibility in the manner in which it accommodates fullerenes. Triamantane, Kelevan, and V-BT do not intercalate in MDMO-PPV, possibly because they do not meet requirements for shape, size, and conjugation. Molecules may need cage-like or spherical shapes and sizes similar to fullerenes in order to intercalate without leaving significant empty space between the side chains. For molecules to intercalate, they may also need conjugation to promote interactions with the conjugated polymer backbones, similar to the interactions between C₆₀ and host conjugated networks.^{38–42} Although triamantane and Kelevan are cage-like molecules, they are somewhat smaller than fullerenes and are not conjugated.³⁴ V-BT

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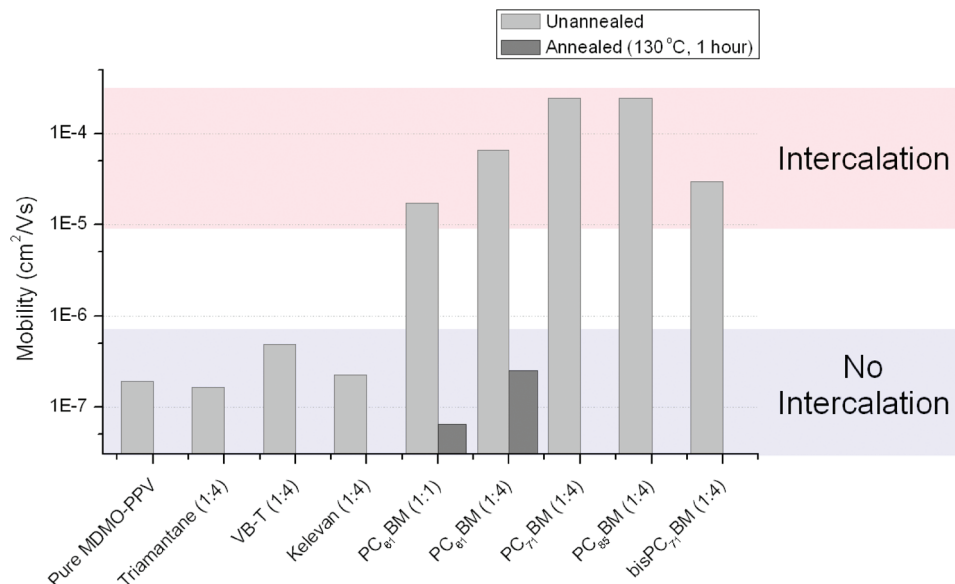


Figure 4. Summary of the SCLC hole mobility measurements for pure MDMO-PPV and unannealed (light gray) and annealed (130 °C for 1 h) (dark gray) MDMO-PPV:molecule blends. The ratios in parentheses represent the MDMO-PPV:molecule weight ratios for the blends.

is conjugated, but its planar shape might prevent it from intercalating. A more detailed discussion of what governs which polymer:molecule blends exhibit intercalation will be presented in an upcoming paper.

To further clarify the relationship between phase separation and enhanced mobilities, we annealed MDMO-PPV:PC₆₁BM blends, because others have observed phase separation in annealed MDMO-PPV:fullerene blends.^{43–45} Annealing 1:1 MDMO-PPV:PC₆₁BM blends for 1 h at 130 °C resulted in phase separation as observed in the SEM (Figure 3h) and a decrease in the hole mobility to a value close to that of pure MDMO-PPV (Figure 4). 1:4 MDMO-PPV:PC₆₁BM blends also exhibited a significant decrease in the hole mobility and incomplete PL quenching (Figure 2) upon annealing. These results provide further evidence that the increase in mobility of MDMO-PPV upon mixing with PC₆₁BM is due to intercalation.

In addition to affecting hole transport in MDMO-PPV:PC₆₁BM blends, intercalation may also affect geminate recombination. Mihailetchi et al. used a model based on Onsager's theory of geminate recombination⁴⁶ that was modified by Braun⁴⁷ to show that poly(3-hexylthiophene) (P3HT):PC₆₁BM, which does not exhibit intercalation,¹⁶ has a higher separation efficiency for photogenerated excitons and a larger initial electron–hole separation

distance than MDMO-PPV:PC₆₁BM.^{48,49} Intercalation may be responsible for this difference, because exciton splitting occurs differently in intercalated and nonintercalated blends. Excitons split inside an intercalated phase produce two oppositely charged carriers in close proximity to each other and within the same phase, an electron on the intercalated fullerene and a hole on the conjugated polymer backbone. The insulating side chains that surround the intercalated fullerenes may hinder the extraction of electrons out of the intercalated phase. On the other hand, excitons in nonintercalated blends split only at the interface between two different phases, a polymer phase and a fullerene phase. Thus, electrons and holes occupy two completely different phases, and the electrons, which are no longer surrounded by insulated side chains, may more easily separate from the holes. Electrons and holes in intercalated blends like MDMO-PPV:PC₆₁BM may therefore be more likely to undergo geminate recombination than those in nonintercalated blends such as P3HT:PC₆₁BM.

Conclusions

Our results indicate that MDMO-PPV:molecule blends can be assigned to two categories. The first category includes MDMO-PPV blends with triamantane, Kelevan, and V-BT and annealed MDMO-PPV:PC₆₁BM blends, which have mobilities close to that of pure MDMO-PPV and exhibit phase separation in polymer-rich blends. These blends do not mix at the molecular level and therefore do not exhibit intercalation. The second category includes unannealed MDMO-PPV blends with PC₆₁BM, PC₇₁BM, PC₈₅BM, and bisPC₇₁BM. The hole mobilities of these blends are several orders of magnitude higher than the hole

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mobility of pure MDMO-PPV. These systems exhibit no phase separation in polymer-rich blends and nearly complete PL quenching. Thus, the formation of a molecularly mixed phase, which is likely an intercalated phase, appears to be responsible for the significant increase in hole mobility of MDMO-PPV when blended with PC₆₁BM, PC₇₁BM, PC₈₅BM, and bisPC₇₁BM. Molecular modeling, which is beyond the scope of this paper because of the complexity of the amorphous structure, may provide further evidence to support intercalation in MDMO-PPV:fullerene blends.

These results have implications for future research on organic light emitting diodes (OLEDs) and organic solar cells. OLEDs would benefit from the increased mobility of MDMO-PPV intercalated with a molecule that does not accept electrons. Although the importance of intercalation in crystalline and semicrystalline polymer:fullerene blends for organic solar cells has been established, this paper introduces the first example investigating the importance of intercalation in amorphous blends.^{16,17} Intercalation is likely to play a significant role in other amorphous blends and should be studied because it can

be controlled by adjusting various polymer and fullerene parameters such as fullerene size, side-chain spacing, and side-chain branching.

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Supporting Information Available: Calculations of the fullerene concentrations for the pure intercalated phase and optimal solar cell performance, PL measurements of MDMO-PPV:triamantane and MDMO-PPV:Kelevan blends, and SEM images of 4:1 MDMO-PPV:molecule blends (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org/>.