Self-Assembling Fullerenes for Improved Bulk-Heterojunction Photovoltaic Devices

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The recent dramatic increase in the cost of fossil fuels has generated a strong resurgence of interest in renewable solar energy sources. Although highly efficient, inorganic photovoltaic devices are costly. Advances in organic “bulk heterojunction” (BHJ) photovoltaic cells have opened prospects for the development of less expensive, easily produced alternatives. To date, the efficiencies of organic BHJ cells have reached 5–6%, still short of the ca. 10% required for commercialization.

The most efficient BHJ devices have been based on conjugated semiconducting polymers blended with a fullerene derivative that serves as an electron acceptor to split excitons created when the polymer absorbs light. These two components must be mixed together on a length scale that is shorter than the exciton diffusion length, typically ca. 10 nm, to ensure that all excitons are harvested. It is also necessary that the polymer and fullerene components form a bicontinuous interpenetrating network for efficient carrier transport of the separated charges. Creating an optimal BHJ is a delicate balancing act: having the components blended too well prevents the formation of separate polymer and fullerene networks, but too much phase segregation leads to the formation of interconnected islands that can act as carrier traps. Indeed, low carrier mobilities in BHJ networks remain the major obstacle for improving device efficiency. Thus, the key to improving BHJ devices is controlling the nanometer-scale morphology of the interpenetrating organic networks.

Several groups have presented methods for controlling the nanoscale morphology of polymer/fullerene blends based on macroscopic device-processing conditions. These include thermal annealing, solvent-vapor treatments, and the use of solvent additives that preferentially dissolve the fullerene. Here, we propose a molecular approach to the control of both the length-scale of polymer/fullerene phase segregation and the electron mobility in the fullerene network. Our method is based on replacing conventional fullerene electron acceptors, such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), with self-assembling fullerene derivatives that may form one-dimensional (1-D) wire-like domains within the active layer. Specifically, we examine a pair of fullerene derivatives that are chemically nearly identical (1a and 1b) but whose molecular shapes either promote or hinder the formation of 1-D stacks. We find that even with identical processing conditions, the nonstacking fullerene 1b gives poor performance in solar cells based on blends with regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) but that the stacking fullerene 1a leads to enhanced photovoltaic efficiency.

The new fullerene adducts 1a and 1b are related to those synthesized by Nakamura and co-workers, who have developed a highly regioselective and efficient penta-addition of aryl copper reagents to C60 that produces molecules with “shuttlecock”-like shapes (Scheme 1). An intriguing feature of these molecules is that some of them tend to form columnar motifs in the solid state, in which the curved surface of one fullerene nestles inside the cavity produced by the five arms of the adjacent molecule. In a future study of the crystal structures of 20 of these adducts, we will show that modification of the substituent arms allows control over their propensity for stacking. Here we focus on BHJ solar cells prepared from 1a and 1b, with the goal of understanding how molecular control over fullerene–fullerene interactions might translate into a more favorable BHJ morphology and thus improve electron mobility and photovoltaic device performance.

The molecular design of fullerene shuttlecock adducts for use in BHJ solar cells is challenging for a number of reasons: the fullerene molecules must have a propensity to self-assemble into desirable structures and display high solubility in solvents used for device fabrication, two properties that are often mutually exclusive. To determine the optimal geometry of a shuttlecock that is likely to stack efficiently with short fullerene–fullerene contact distances, we performed a series of molecular modeling calculations (AM1, Spartan 04). These calculations indicated that the introduction of the large tert-butyl group at the para-position of each of the phenyl substituents produces a deep, well-shaped cavity that should promote self-assembly. We thus synthesized compound 1a and found that the addition of the para tert-butyl groups makes 1a an efficient self-assembly 1-D “stacker” that also is suitably soluble in o-dichlorobenzene (ODCB).

Following the general procedure of Nakamura et al., we obtained 1a as a bright red solid and purified by column chromatography on silica gel. Figure 1 shows the X-ray structure of 1a obtained by slow diffusion of n-pentane into a saturated solution of 1a in 1-chloronaphthalene. In this structure, the fullerenes form 1-D stacks that are aligned antiparallel and separated by sheaths of n-pentane molecules. The distance between fullerene centroids within each column is 10.83 Å, and the shortest distances between fullerene centroids in adjacent columns are 14.85 and 15.86 Å.

We also examined the crystal structures of 1a crystallized from ODCB, CS2, and C6H5Cl and found 1a is a “universal stacker”: crystals of 1a display a packing motif characterized by the assembly of 1-D fullerene stacks that is solvent-independent. For the four solvents we examined, it appears that the overall packing structure is dictated by the self-assembly of the 1-D stacks and that the solvent molecules simply fill in the voids.
An identical motif is observed in the crystal structure of
Figure 2a) and 9.894 Å (hexagon
atoms are removed for clarity in all structures above.
with solvent molecules shown in space-filling representation. Hydrogen
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with
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Figure 2a,b shows the
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reside just within the cavity formed by the five
centroid
and the fullerene-solvent units form a close-packed 3-D diamond-
organization and/or crystallinity of the
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Clearly, the packing of 1a contrasts greatly with that of 1b,
in which subtle changes in the solvent produced entirely different
structural motifs. The difference can be rationalized on the basis of
molecular shape: the deeper cavity of 1a resulting from para-
substitution promotes efficient 1-D stacking, while the meta-
substituted phenyl arms of 1b produce only a shallow cavity.
An ideal BHJ solar cell should have two networks that are both
continuous and fully interconnected throughout the thickness of
the active layer. For polymer/fullerene-based BHJ solar cells, a
fullerene derivative with a propensity to form 1-D stacks may form
a more ideal network than one that makes isotropic aggregates that
could more easily lead to island formation. To test this idea, we
fabricated BHJ solar cells from blends of either 1a or 1b with
P3HT.8 Although we do not necessarily expect these blends to
contain fullerene aggregates with structures identical to those shown
in Figures 1 and 2, it seems likely that the robust stacking and
nonstacking molecular motifs found in the single crystals also will
be present in the devices.

Because the reduction of the local symmetry of a group tends to
increase overall molecular solubility, we also investigated the 3-tolyl
system 1b: the solubility of this molecule in ODCB is ca. 10 mg/
ml, which is high enough for the ready fabrication of devices by
spin-coating from a concentrated solution of this fullerene mixed
with P3HT. Crystals suitable for single-crystal X-ray diffraction
were grown from five different solvent systems, resulting in very
different extended crystal structures.10 Figure 2a,b shows the
packing structure of compound 1b·CHCl3 grown from a concen-
trated solution in a CHCl3/CS2 mixture. The chloroform molecules
reside just within the cavity formed by the five meta-tolyl groups,
and the fullerene-solvent units form a close-packed 3-D diamond-
like network in which each fullerene has four near-neighbors
arranged in an approximately tetrahedral geometry. The fullerene
centroid–centroid distances are 10.436 (edge–vertex close contacts,
Figure 2a) and 9.894 Å (hexagon–hexagon, Figure 2b), respec-
tively. An identical motif is observed in the crystal structure of
1b·CS2, grown by slow diffusion of n-pentane into a CS2 solution
of 1b. In contrast, 1b·1,2-C6H4Cl2 (Figure 2d,e) forms a layered
structure.10 Although the cocrystallized ODCB molecules reside
just within the cavity in a similar fashion to 1b·CHCl3, alternating
layers of fullerene and solvent are observed with a periodicity of
16.55 Å (Figure 2e). The fullerenes within each layer are roughly
hexagonally packed, and each fullerene has five near-neighbors (C60
centroid–centroid distances ≤ 10.193 Å). Nearly identical packing
is observed for 1b·C6H5CH3 (slow evaporation of PhCH3).10
However, the crystal structure of 1b·(C6H5Cl)1.875 is very different,
with each fullerene having three near-neighbors (C60centroid–centroid
distances ≤ 10.318 Å), forming a layered, puckered, honeycomb
network (Figure 2c).10 These diverse structures make it clear that
1b does not tend to form 1-D stacks, so we shall use it as a model
nonstacking shuttlecock.

A comparison between the current density—voltage (I–V) character-
istics of as-cast P3HT:1a and P3HT:1b devices11 under simulated
AM1.5 solar irradiation8 is shown in Figure 3a,b. The I–V curves
show that both the short-circuit current density (Isc) and open-circuit
voltage (Voc) are larger for the devices fabricated with 1a. The larger
value of Voc for 1a is consistent with the idea of this stacking shuttlecock
producing a more interconnected network compared to 1b. The
difference in Voc is less straightforward to interpret. The value of Voc
is thought to depend only on the difference of the donor HOMO and
acceptor LUMO energies,12 but these devices use the same donor and
the LUMO levels of 1a and 1b are nearly identical. Thus, the difference
must be related to the nm-scale morphology of the fullerene network.
One explanation is that the different fullerene networks have different
densities of charge-carrier traps, which contribute to the space-charge
buildup and thus affect the built-in potential in the device. Alternatively,
the different fullerene aggregation geometries may affect the self-
organization and/or crystallinity of the

Figure 1. Crystal structure of 1a·(C6H12), (a) Antiparallel a-axis stacks,
viewed along the (a) bc plane and (b) a-axis. Hydrogens are removed for
clarity; n-pentane solvent molecules are shown in space-filling mode.

Figure 2. Crystal structure of 1b·CHCl3, (a) ac layer, viewed along the
b axis, with disordered CHCl3 solvent shown in space-filling representation.
(b) Single b-axis chain, viewed along the a axis. Carbon atoms with close
contacts (3.412–3.551 Å) are highlighted. (c) Crystal structure of
1b·(C6H5Cl)1.875. Single bc layer, viewed along the a axis, with selected
solvent molecules shown in space-filling representation. (d) Crystal structure of
1b·C6H4Cl2. Single bc layer, viewed along the a axis, with the solvent
removed for clarity. (e) bc Layers for 1b·CHCl3 viewed along the b axis,
with solvent molecules shown in space-filling representation. Hydrogen
atoms are removed for clarity in all structures above.

Figure 3. (a) I–V curves for as-cast and thermally annealed BHJ solar
cells made from a 1:0.35 blend of 1a and P3HT. Annealing of these cells
also occurs rapidly, with significantly improved device efficiencies compared
to the data in (b). (b) I–V curves for as-cast and thermally annealed BHJ
solar cells made from a 1:0.45 blend of 1b and P3HT. Annealing of these
cells is complete in 5 min, but the overall device performance is low.

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crystallinity or average conjugation length could be reflected in the spatially averaged HOMO of the polymer, thereby directly affecting $V_{oc}$.

Since thermal annealing frequently improves the efficiency of polymer-based BHJ solar cells, we chose to anneal our solar cells based on blends of P3HT with 1a or 1b under conditions similar to those used to improve the efficiency of P3HT:PCBM solar cells. As with P3HT:PCBM devices, annealing our devices based on 1a and 1b decreased $V_{oc}$ but increased $I_{sc}$, leading to an overall increase in efficiency (Figure 3). The reduction in $V_{oc}$ is generally assigned to reduced space-charge buildup while the increase in $I_{sc}$ is related to improved network formation. We find that the annealing-induced increase in $I_{sc}$, which is the most direct indicator of the underlying network structure, is less than half as large for 1b compared to 1a. Since the electronic structures of these two fullerenes are essentially identical, the larger improvement in photovoltaic performance upon annealing devices based on tert-butyl system 1a must be associated with the increased self-organization of this fullerene derivative.

Thermal annealing is a kinetically slow process that requires the diffusive motion of molecules. Indeed, P3HT:PCBM devices show a steady improvement in performance with thermal annealing for ca. 20 min, after which time the performance plateaus. This large improvement does not occur for devices that have been subjected to “solvent annealing” by casting from slow-evaporating solvents since thermal annealing frequently improves the efficiency of PCBM:PhCl (≤ 2.902 Å) and PCBM:OxDC (≤ 3.171 Å); this high degree of contact should greatly favor electron mobility. Even with the high propensity of 1a to form columnar stacks, the closest fullerene—fullerene contacts in the crystal structures are relatively long (≥ 4.035 Å, 1a·(C$_5$H$_5$)$_2$). We attribute this both to the repulsive interaction between meta-aryl hydrogens of the shuttlecock “feathers” with the neighboring fullerene ball, which prevents closer approach of molecules along the stacks, and to the interstack steric crowding by the “feathers” that keep individual columns well separated. The shuttlecock system, however, allows for incredible chemical diversity within a single molecular motif. We are thus currently exploring crystal structures and BHJ device behavior of a large range of penta-substituted fullerene derivatives with the goal of improving BHJ solar cell efficiency by simultaneously optimizing the propensity for fullerenes to stack, the fullerene—fullerene contact distances, and the degree of phase segregation with conjugated polymers.

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**Supporting Information Available:** Experimental procedures, spectra and CIF files for 1a·(C$_6$H$_5$)$_2$, 1b·C$_6$H$_5$CH$_3$, 1b·(C$_6$H$_5$)$_2$Cl, 1b·1,2-C$_6$H$_4$Cl$_2$, 1b·CHCl$_3$, 1b·CS$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

9. X-ray data for 1a·(C$_6$H$_5$)$_2$. Red platelet (0.3 x 0.2 x 0.2 mm$^3$) from 1-chloronaphthalene/C$_5$H$_12$. Space group: Pnma; $a = 22.721(4) \text{Å}$; $c = 17.128(4) \text{Å}$; $V = 8430(2) \text{Å}^3$; $Z = 4$; $T = 100(2) \text{K}$; $N_{u}$ (unique) = 11 521; $R_{1} = 0.076$; $R_{w} = 0.196$.
10. X-ray data for 1b·CHCl$_3$. Red platelet (0.4 x 0.1 x 0.1 mm$^3$) from CHCl$_3$/CS$_2$. Space group: Pnma; $a = 18.298(5) \text{Å}$; $b = 17.955(5) \text{Å}$; $c = 17.352(5) \text{Å}$; $Z = 4$; $T = 100(2) \text{K}$; $N_{u}$ (unique) = 7727; $R_{1} = 0.077$; $R_{w} = 0.200$. 1b·C$_6$H$_5$Cl. Red prism (0.2 x 0.2 x 0.2 mm$^3$) from CS$_2$/CH$_3$I. Space group: Pnma; $a = 18.311(5) \text{Å}$; $b = 17.965(4) \text{Å}$; $c = 17.344(5) \text{Å}$; $Z = 4$; $T = 100(2) \text{K}$; $N_{u}$ (unique) = 7858; $R_{1} = 0.063$; $R_{w} = 0.171$. For 1b·1,2-C$_6$H$_4$Cl$_2$, 1b·CH$_2$Cl$_2$, and 1b·(C$_6$H$_5$)$_2$Cl, see Supporting Information.