Using Self-organization to Control Morphology and Improve the Efficiency of Solar Cells

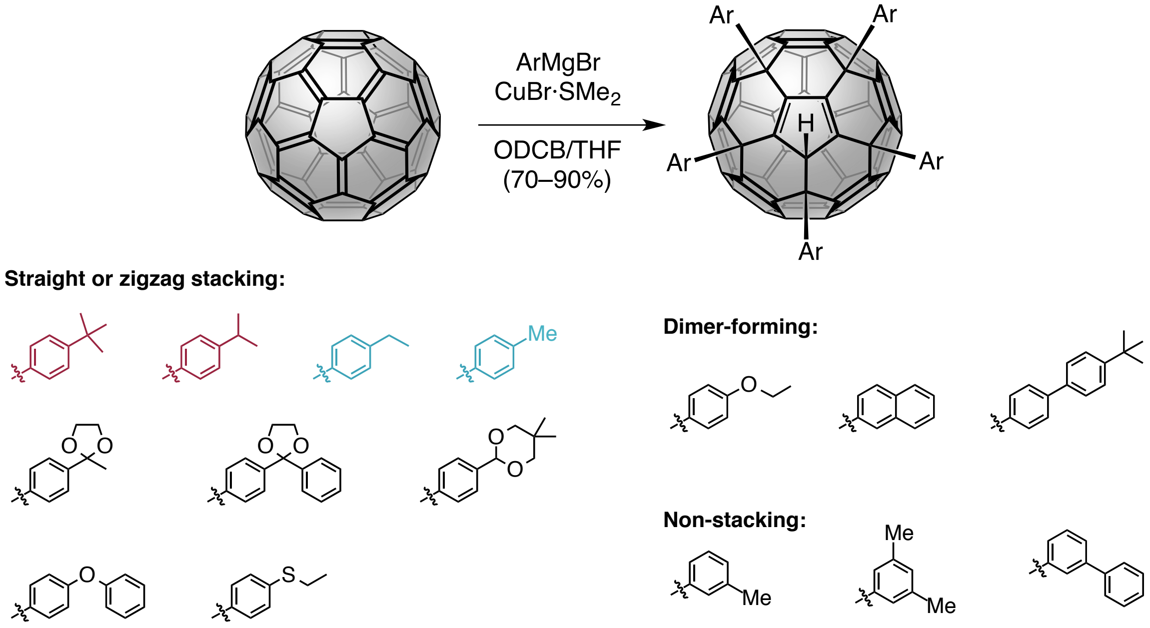
Pentaaryl shuttlecocks

Supramolecular donor-acceptor assemblies have exciting potential for photovoltaic applications due to the formation of intimate contacts between the donor and acceptor molecules, fostering efficient charge transfer. There is currently a large effort aimed at designing molecules (usually donor-acceptor dyads) that undergo photoinduced charge transfer with long-lived charge separation. In most systems, the typical charge separation lifetime is μs, and in a few cases, separated charges can live to the ms time scale. This is obviously mediocre to what is achieved in biological photosynthesis, where the photogenerated charges effectively never recombine, giving the photosynthetic reaction center an essentially perfect quantum yield.

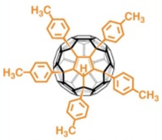
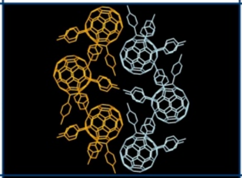
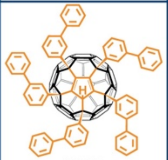
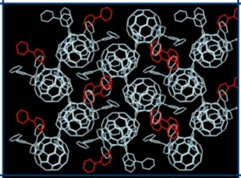
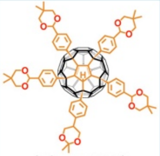
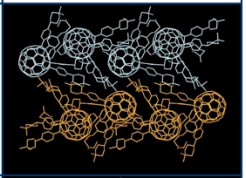
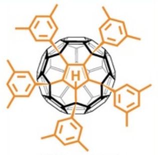
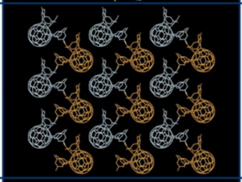
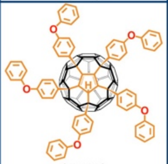
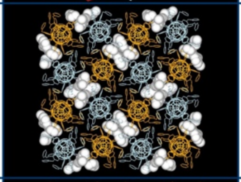
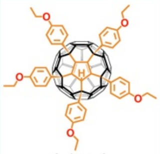
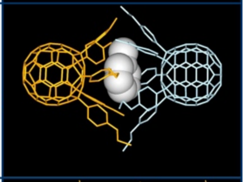
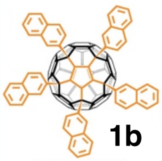
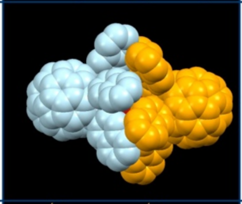
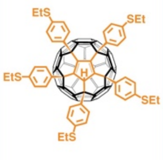
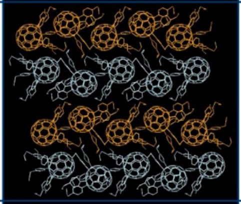
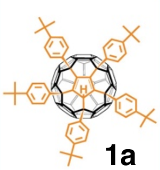
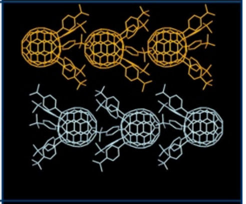
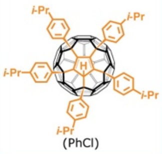
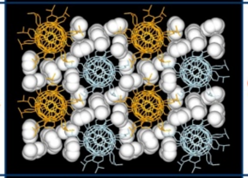
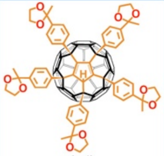
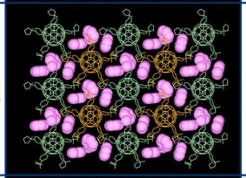
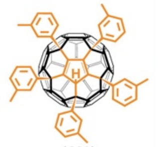
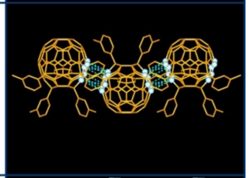
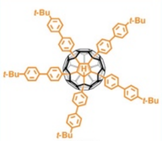
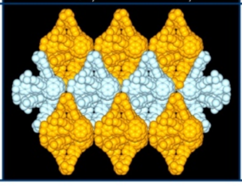
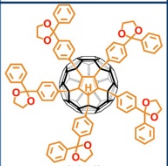
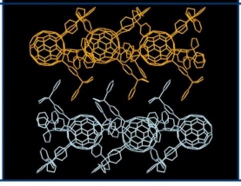
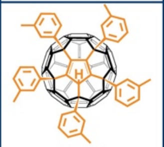
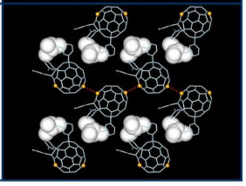
In a long-standing and highly fruitful collaboration with my inorganic and physical chemistry colleagues Sarah Tolbert and Benjamin Schwartz at UCLA, we have studied novel approaches to organic solar cells with the ultimate aim to raise their photogenerated current efficiency.[1,2] In particular, self-assembling fullerene derivatives were investigated for their propensity to create robust, thermodynamically-driven nanoscale architectures in polymer/fullerene blends.[3-9] Although self-assembly can clearly help device performance,[2,8] the efficiency of devices made with assembling fullerenes will only surpass those made with non-assembling fullerenes if the self-assembly process can also foster high carrier mobility.[2,8] We investigated self-assembling pentaaryl shuttlecocks to improve bulk-heterojunction photovoltaic systems ("plastic solar cells"). A series of pentaaryl fullerenes ("shuttlecocks" or SCs) were synthesized as electron acceptors using the convenient methodology developed by Nakamura (Table 1). The importance of molecular shape and crystal packing properties of the fullerene acceptor on the performance of PV devices was examined.[2,3,7,8] The best performance came from devices fabricated with *t*-butylphenyl derivative **1a** that displays a very robust and solvent-independent anisotropic packing motif in the solid state, forming one-dimensional columnar "stacks". A series of thirty X-ray structures described in a full paper gives a general view of the self-assembling trends of these molecules.[3]

Table 1. a) General Shuttlecock Synthesis, Aryl Groups Investigated, and Types of Packing Modes in the Crystal. b) List of Shuttlecock Structures and Their Experimentally Determined Packing Structures.

a)



b)

Structure (Crystallization Solvent)	Packing Structure	Structure (Crystallization Solvent)	Packing Structure	Structure (Crystallization Solvent)	Packing Structure
 (ODCB/pentane)		 (CS2)		 (toluene-*i*PrOH)	
 (PhI-pentane)		 (ODCB)		 (toluene)	
 **1b** (CS2 or ODCB)				 **1a**	
 (PhCl)		 (tol)		 (CS2)	
 (CS2)		 (PhCl)		 (CHCl3)	

Key structures are shown on the previous page. Not every shuttlecock system stacks – some derivatives are strongly solvent-dependent in their crystallization modes. Thus, some consistently form dimers such as the pentakis-2-naphthyl shuttlecock **1b** beautifully coordinated through ten edge-to-face C–H$\cdots\pi$ interactions. Within this project, we also discovered an unusual de-arylation reaction of the pentakis(triphenylamine) shuttlecock, which gives a “defeathered” epoxide.[10]

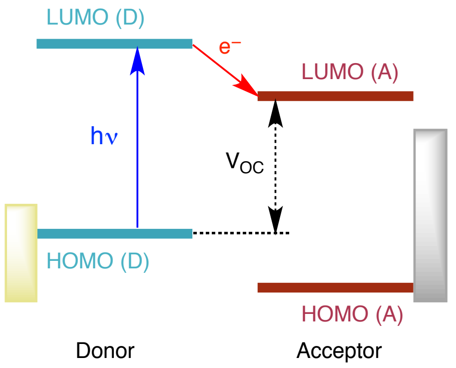


Fig. 1: Relative energy levels of the frontier orbitals for a donor and acceptor in BHJ photovoltaic devices.

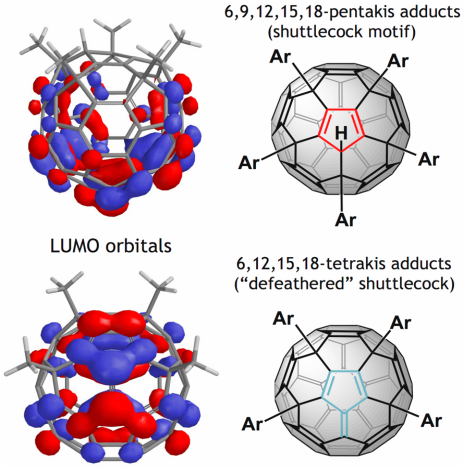


Fig. 2: LUMO coefficients for pentakis- and tetrakismethyl shuttlecocks.

Tetraaryl shuttlecocks

Additional work on this project has focused on synthesizing fullerene derivatives with a decreased LUMO level relative to the pentaaryl shuttlecocks, but which are still prone to self-assemble into columnar structures. We have been aiming at better matching the LUMO energy levels of our fullerene derivatives with those of electron-donating polymers (Fig. 1). The difference between the LUMO levels of the electron-donating and electron-accepting molecules in bulk-heterojunction (BHJ) devices should ideally be downhill by ~0.5 eV to achieve the most efficient electron transfer after photoexcitation. Additionally, the gap between the LUMO of the electron-accepting molecule (fullerene derivative) and the HOMO of the electron-donating polymer should be as large as possible to maximize the open-circuit voltage (V_{OC}) of the device (Fig. 1). The latter influences the efficiency of the device as shown by the equation for photovoltaic efficiency (η):

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$

where J_{sc} is the short circuit current, FF the fill factor, and P_{in} is the incident radiant power (typically the sun at earth’s surface).

As referenced above, our stacking five-feathered shuttlecocks (SCs) show relatively low photovoltaic device efficiencies, in part because there is inefficient LUMO–LUMO contact between shuttlecock units within stacked assemblies (Fig. 2, top). However, four-feathered (or “defeathered”) shuttlecocks can address this issue: The fulvene subunit in these shuttlecocks (teal color, Fig. 2, bottom) localizes LUMO orbitals over the entire fullerene moiety, and especially in the bowl region between the four feathers, in striking contrast to five-feathered shuttlecocks that have no LUMO density in this region. We have recently developed two syntheses to this new system, including one based on a novel methodology.

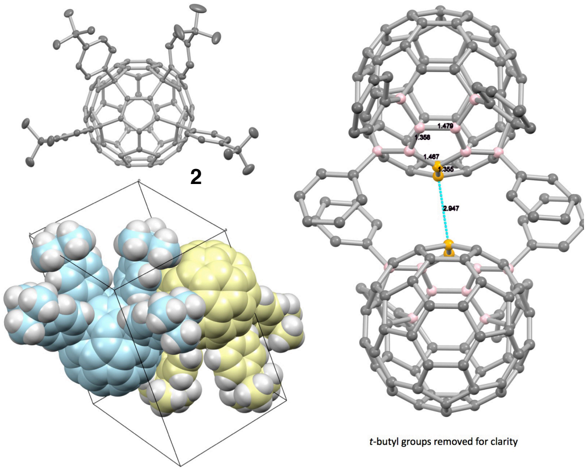


Fig. 3: Crystal structure of our first 4-feathered SC (**2**).

This new methodology is based on a novel defeathering reaction of five-feathered shuttlecocks by taking advantage of the radical fragmentation of benzylic groups on the fullerene surface.[10] We have also achieved a stepwise aryl group addition protocol (not shown) that has provided our first fully characterized tetrakisadduct **2** (Fig. 3). We are currently optimizing the yields of these reactions to prepare large amounts of material needed to test in OPV devices.

Surprisingly, the crystal structure of tetrakisadduct **2** shows a very short contact C–C distance (2.947 Å) between the fulvene carbons of two molecules in head-to-tail relationship, indicating significant interaction between them (Fig. 3). Furthermore, these molecules are not stacked as expected, although there are several additional short C–C distances in the packing structure that should promote electron hoping in photovoltaic devices. Finally, crystallization of tetrakisadduct **2** from a MeOH/$CHCl_3$ mixture at 25 ˚C affords the methanol reaction product **3** (Fig. 4), whose packing structure now reveals a stacked situation!

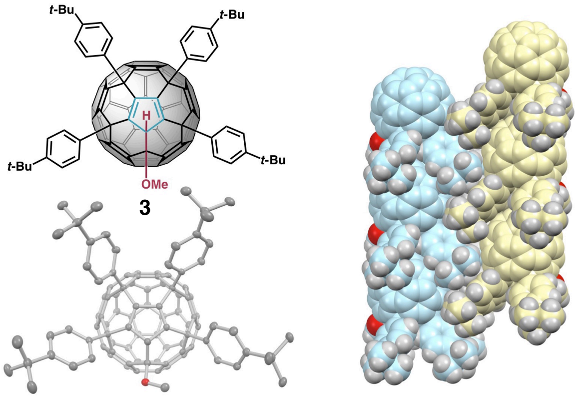


Fig. 4: Crystal structure and packing mode of the methanol adduct **3**.

1,4-Bisbenzyl derivatives for Improved Electron Mobility and a Higher Open-Circuit Voltage

The results of our work on self-assembling fullerenes indicate that an ideal fullerene acceptor must possess high local electron mobility – resulting from good LUMO overlap between adjacent fullerenes in the solid – and high macroscopic mobility by forming a good network through self-assembly.[8] There have been only a few reports of fullerenes in polymer-based photovoltaics (PVs) that improve upon PCBM. Recently, we obtained excellent results by synthesizing a new series of fullerene 1,4-bisadducts, which possess higher-lying LUMOs compared to PCBM, as well as strongly spread out LUMO orbitals similar to PCBM. They are also compatible with high-performance, near infrared-absorbing polymers like PTB7, which is not always the case with other fullerene derivatives. The 1,4-bisadducts were prepared by the reaction of $C_{60}{}^{2-}$ with substituted benzyl bromides in MeCN or benzonitrile to give 1,4-bisbenzyl adducts **51a-k** bearing uniform or mixed substituents (Fig. 5). Benzylation of the intermediate monoadducts provided the *mixed* 1,4-bisadducts **51f-k**, as summarized in Fig. 5. We fabricated BHJ solar cells by blending P3HT with each of the 1,4-bisadducts in Fig. 5. When both phenyl groups were substituted by two methoxy groups (**51e**), P3HT-based OPVs with matched polymer and fullerene composition and film thickness showed superior performance to P3HT:PCBM; devices with **51e** had a ~20% higher PCE and a V_{OC} of ~0.7 V. We also fabricated BHJ solar cells with **51e** and PTB7[11] to test the compatibility of such fullerene derivatives with

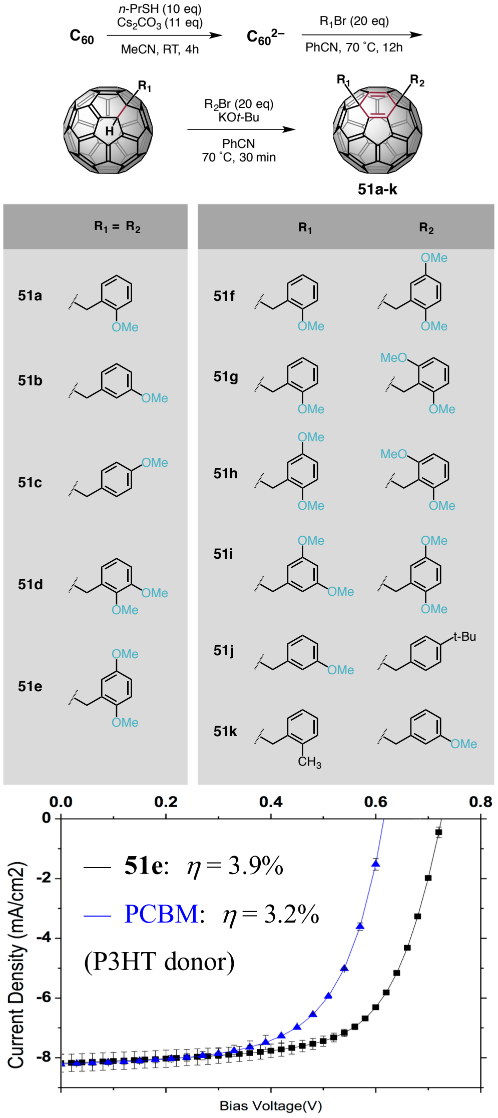


Fig. 5: Synthesis of 1,4-bisadducts and *J-V* curves of P3HT-based BHJs with **51e** (blue), showing higher efficiency than PCBM (black).

a state-of-the-art near infrared-absorbing polymer, and found comparable performance to $PC_{60}BM$. We are currently working to further enhance electron transfer, to use the high LUMO levels of 1,4-bisbenzyl adducts such as **51e** that lead to increased V_{OC}, and to take advantage of the easy-to-synthesize nature of these 1,4-bisadducts to fabricate high-PCE polymer solar cells.

Self-Assembling Polymers for Control Over Nanoscale Photovoltaic Morphology in Aqueous Solutions

Biological photovoltaic systems are fundamentally characterized by the remarkable energy quantum efficiency in which nature converts sunlight into chemical energy. This results from the exquisite organization of photoactive elements that promote rapid movement of charge carriers out of a critical recombination range. We have been investigating molecular materials that could mimic this process of self-assembly, charge separation, and charge collection in water.[1,12,13] For this purpose, we modified the backbone of a traditional semiconducting polymer, poly(fluorene-alt-thiophene) (PFT; Fig. 6a), with cationic side-chains so that they can self-assemble in aqueous solution (Fig. 6a).[12] These systems form micellar bundles of conjugated polymers (Fig. 6b-d) which can be loaded with two types of cationic fullerenes, one that locates in the inner location of the micelles, and the other in the outer, thus serving different and critical roles in the photoinduced charge transfer cascade. The first type of charged fullerene inserts into the micelle, next to the conjugated polymer backbone, so that the initial photoinduced charge separation is rapid (≤ 1 ps). The second type of fullerene assembles in the gallery region of the micelle, where it can accept a charge from the first fullerene type, and then stabilize that charge due to the high reorganization energy of water molecules surrounding the micelle. Surprisingly, we found that photogenerated separated charges in this system are stable for extended periods of time to give solutions with a dark green color typical of the radical cation left on the polymer backbone. In fact, this charge-separated state persists for *weeks* after exposing the solution to light.[13] The fact that we are able to make these long-lived separated charges in aqueous solution with relatively small variations on standard organic photovoltaic materials has opened a vast array of possibilities for using electron transfer cascades for reduction chemistry or water-processable ‘green’ solar cells.

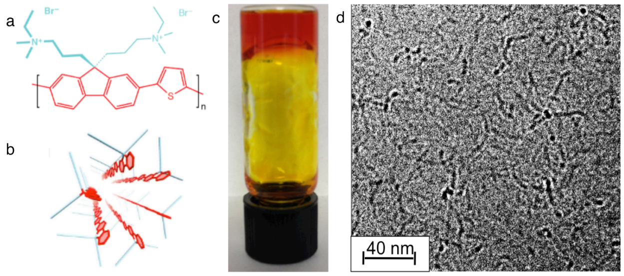


Fig. 6: a) PFT structure. b) Cartoon of a self-assembled PFT micelle. c) Upside-down vial of PFT hydrogel. d) Cryo-TEM of PFT micelles showing the micellar bridging behavior at dilute concentrations (1 mg/mL).

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