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The Structural Origin of Electron Injection Enhancements with Fulleropyrrolidine Interlayers

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Supporting Information

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Abstract

The orientation of the substituent groups in a new class of work function modification layers, based on functionalized fulleropyrrolidines, is measured and found to directly account for the sign of the work function change.

Graphical Abstract

Keywords

electronic structure; zwitterion; amine; C₆₀; electron injection layer

Market demand for high functionality products at low cost (the internet of things) drives the development of solution processing techniques for electronic devices. Optimal performance in transistors, diodes, or receivers (both solar cells and detectors) critically depends on efficient charge injection and extraction at contacts. For traditional, high temperature processed semiconductors, this is achieved by creating ohmic contacts via doping by diffusion or implantation. For most solution processed semiconductors, charge injection is

controlled by band alignment between the contact and active layer and the hole/electron injection barrier (HIB/EIB) is determined by the energetic difference between the Fermi level (E_F) of an electrode and the transport level of the semiconductor.^[1, 2] This has led to considerable research in solution processable work function modifiers (WFMs) for use as both hole injection layers (HILs)^[3–6] and electron injection layers (EILs).^[7–10]

EILs represent a significant fundamental challenge, since the oxidative stability of low work function (WF) materials efficient at electron injection is problematic. Nonetheless, a chemical paradigm for EIL fabrication has developed in recent years. Polyelectrolyte modifiers can increase or decrease the WF of an electrode, depending on which counterions are introduced.^[6, 11, 12] However, the presence of mobile ions may be deleterious to device stability.^[13, 14] Therefore, counterion-free zwitterionic polymers have been examined as WF reducers.^[15–18] We reported poly(sulfobetaine methacrylate) (PSBMA) interlayers to reduce the WF of a wide range of electrodes (metals, oxides, polymers) by more than 1.0 eV in inverted organic electronic devices.^[15] However, the thickness of the WFM was limited to less than 8 nm due to its insulating properties. The use of conjugated polymers to improve mobility is complicated by their typical p-type character.^[19] To overcome this limitation, it is desirable to develop n-type semiconductor backbones with appropriate functionality. In addition to modifiers with localized charges, highly polar neutral functional groups, such as amines, have been used successfully in EILs.^[8]

Although WFMs significantly improve device performance, a molecular level understanding is still lacking. For example, n-doping reactions by impurities are reported following polyethylimine (PEI) vapor treatment on poly(3,4-ethylenedioxythiophene):polystyrene sulfonate, PEDOT:PSS,^[20] in contrast to the commonly adopted interfacial dipole mechanism for WFM of PEI.^[8] A basic understanding of the arrangement of substituent groups and resultant interface electronic structure is necessary to guide the synthesis of new WFMs and to optimize their use in improving device performance.

Shown in Scheme 1 are the structures of the tris(dimethylamino), C_{60} -N, and tris(sulfobetaine), C_{60} -SB, substituted fulleropyrrolidine molecules studied in this work as WFM and EIL layers (detailed syntheses are described in ref. 18). The C_{60} core should impart significant electron mobility, allowing thick coatings to perform efficiently, while incorporating the established amine or zwitterion functionality of successful EILs. C_{60} -N and C_{60} -SB were first demonstrated as effective WFMs in conventional OPV devices of the structure: ITO|PEDOT:PSS|active layer|WFM|Metal, where ITO is indium tin oxide and a high performing polymer-fullerene bulk heterojunction (BHJ) served as the active layer.^[18] Both fulleropyrrolidines were effective WFMs, allowing high efficiency devices to be fabricated with high WF noble metals (Au, Ag, Cu) as the electron extraction cathode without the requirement of vapor deposition of air-sensitive LiF or Ca WFMs. When used with Ag cathodes, it was found that films ~8 nm of C_{60} -N pinned the cathode WF at ~3.65 eV, while similar films of C_{60} -SB pinned the cathode WF at ~3.85 eV. Optimal device performance of ~9% PCE was achieved with ~15 nm of C_{60} -N and a Ag cathode. This represented the best combination of open-circuit voltage (V_{OC}), series resistance (R_s), and optical effects. Recently C_{60} -SB has been demonstrated to be similarly effective in inverted OPV devices of the structure: ITO|WFM|BHJ| MoO_x |Ag^[17] where the fulleropyrrolidines

replaced the ZnO_x or TiO_x sols commonly employed for WFM.^[21] Similar to the performance on metals, C_{60} -SB reduced the WF of ITO to ≈ 4.0 eV. It is remarkable that both fulleropyrrolidines (neutral amine and zwitterion SB) appear equally effective WFMs on both metals and ITO. In this paper, we present detailed electronic structure studies of these fulleropyrrolidines on ITO, identifying their electron affinity (EA), transport gap (E_t), and EIB, all crucial for understanding the electron injection efficiency. This is complemented with detailed orientation and alignment studies of the amine and sulfobetaine (SB) groups with near edge X-ray absorption fine structure (NEXAFS) and vibrationally resonant sum-frequency generation (VR-SFG). We establish that the common mode of action of the materials on both metals and oxides is linked to the interfacial organization of the polar/charged substituent groups.

The electronic structure and band alignment of the WFM layers were probed by ultraviolet and inverse photoelectron spectroscopies (UPS and IPES). Figure 1 shows UPS and IPES spectra of (a) C_{60} -N and (b) C_{60} -SB enabling determination of the E_t . The HOMO and LUMO onsets of C_{60} -N are observed at 1.80 eV below and 0.20 eV above the Fermi level, respectively. Therefore, the E_t of C_{60} -N is estimated to be 2.00 eV. In C_{60} -SB, the HOMO and LUMO onsets are observed at 1.60 eV below and 0.45 eV above the Fermi level, respectively. The approximate E_t of C_{60} -N is 2.05 eV. These values are larger than the reported optical band gap of 1.8 eV from UV-Vis absorption measurements.^[18] Therefore, the exciton binding energies of C_{60} -N and C_{60} -SB are estimated to be (0.2 to 0.3) eV, and this must be considered to when evaluating the EIB of C_{60} -N and C_{60} -SB from the electrode.

Figure 2 shows the thickness-dependent UPS spectra of the secondary electron cutoff (SEC) region and HOMO region of C_{60} -N (0.5, 1, 2, 4, 8, 16) nm films on an ITO substrate. The SEC region spectra were normalized for clarity and shown with respect to the kinetic energies so that the onset directly indicates the WF. The Shirley-type background was removed from the HOMO region spectrum. The WF of ITO was measured to be 4.35 eV. As the C_{60} -N layer thickens, the WF decreases by 0.60 eV and becomes pinned for films thicker than ≈ 4 nm. The HOMO onset of C_{60} -N is observed at 2.00 eV from the E_F at the 4 nm-thick C_{60} -N layer and does not shift when the C_{60} -N layer thickens further.

Figure 3 shows similar UPS spectra of the normalized SEC region and HOMO region of C_{60} -SB (0.5, 1, 2, 4, 8, 16) nm films on an ITO substrate. The behavior is analogous to that of C_{60} -N: the WF decreases with thickness, pinning at ≈ 0.30 eV lower than for clean ITO. The HOMO level of C_{60} -SB is observed at 1.75 eV from the E_F .

Figure 4 shows energy level diagrams for both C_{60} -N and C_{60} -SB on ITO derived from the photoelectron spectroscopies. The ionization energy (IE) and EA of C_{60} -N are 5.75 eV and 3.75 eV, and those of C_{60} -SB are 5.80 eV and 3.75 eV, respectively. Even though the IE and the EA are very similar, the EIBs are slightly different. This originates from their different interface dipole: 0.60 eV for C_{60} -N and 0.30 eV for C_{60} -SB. The alignment of the C_{60} -N LUMO with the ITO E_F is remarkable, and suggests near ohmic contact that should promote facile electron injection.

We note that the WF of a C₆₀ film on ITO is observed to be 4.55 eV (Figure S1), indicating an interface dipole of *opposite sign* to that observed with the substituted fulleropyrroldones (i.e., C₆₀ increases the WF of ITO). Thus the amine and zwitterionic groups on C₆₀ are crucial for determining WFM effects, changing the WF relative to C₆₀ by 0.5 eV. The positions of the saturated bulk WF on ITO for C₆₀-N and C₆₀-SB (3.75 eV and 4.05 eV) are similar to those reported on noble metals (3.6 eV and 3.8 eV),^[18] notable in light of the presumed differences in functional group interactions with oxide vs metal surfaces.

Figure 5 shows the calculated dipole moment of C₆₀-N and C₆₀-SB at the optimized structure from density functional theory (DFT) calculations. The dipole moment is 7.4 D for C₆₀-N and 35.3 D for C₆₀-SB. These large dipole moments originate from the lone electron pair of the amines on C₆₀-N and from the zwitterion dipole of C₆₀-SB. The dipole moment for C₆₀-SB is nominally consistent with the vector sum of the experimental dipole (23 D) of a single SB unit.^[22] The dipole moment for C₆₀-N is significantly larger than expected based on the ≈1 D dipole of the terminal amine. It is notable that the larger WF modification seen for C₆₀-N contrasts the larger dipole of C₆₀-SB. Additionally, the direction of the molecular dipoles differs: the dipole moment is pointing from C₆₀ to the functional groups on C₆₀-N, and is in the opposite direction for C₆₀-SB.

To understand the molecular origin of the interfacial dipoles in Figure 4, one must determine the alignment and orientation of the polar components in the film. Angle-resolved NEXAFS was performed to assess molecular alignment. Shown in Figure 6 is representative data from the C-edge for the two fulleropyrroldines on ITO, measured using total electron yield (TEY) with a surface sensitivity of ≈3 nm. The sharp structure between 284 and 286 eV is due to the π* resonances of the C double bonds in the fullerene cages. The weak structure at higher energies arises mostly from σ* resonances of the C single bonds. The dispersion of intensity with angle-of-incidence can be related to the net alignment ($\langle \cos^2\theta \rangle$, where θ is the tilt from the surface normal) of the relevant transition dipole vector. For a highly polarized beam such as available at the undulator used for these measurements, the experimental dispersion parameter: $D = \frac{I[90] - I[0]}{I[90] + I[0]}$, where I[α] is the normalized intensity at the angle-of-incidence α, can be directly related to the alignment: $D = \frac{4}{1 + \langle \cos^2\theta \rangle} - 3$. Note that positive values of D correspond to transition dipoles on average lying in the plane of the surface, negative values to average upright (along the surface normal) alignments. A value of 0 corresponds to transition dipoles being isotropically oriented or to the special case where the transition dipoles have a narrow orientation distribution along the so-called magic angle of 54.7° with respect to the surface normal. For the spherical C₆₀ molecule, no dichroism is expected (D = 0) due to the σ and π bonds being on average isotropically oriented (spherical symmetry), however transitions associated with the amino and SB sub-units may still produce measurable dichroism. Table 1 summarizes the D parameter for both the π* and σ* regions of the spectrum for ≈10 nm films of C₆₀-N and C₆₀-SB on both ITO and Au substrates (see Figure S2 for NEXAFS data of films on Au substrates). Very little dichroism is observed in the NEXAFS spectra of C₆₀-N and C₆₀-SB, with D values close to 0 for both π* and σ* regions. The lack of dichroism in the spectrum of C₆₀-N is attributed to the C₆₀ unit dominating the spectrum of C₆₀-N. However, a strong preferential orientation (lying flat vs standing up) of the amino groups should nevertheless present detectable dichroism. For

C₆₀-SB, the NEXAFS spectrum is substantially different than that of C₆₀, due to the larger SB groups; the lack of strong dichroism is direct evidence of a lack of a strong preferential orientation of the SB groups with respect to the substrate. While this could point to a glassy, amorphous film (analogous to substituted [6,6]-phenyl-C₆₀ butyl acids methyl ester (PCBM),^[23] which forms a glassy, amorphous film when deposited by spin-coating) there could still be molecular orientation that is not easily detected by NEXAFS, such as the linear substituents arranging themselves with an orientation close to the magic-angle, with the ends of the amino and SB groups on average pointing either away from or toward the substrate.

To fully understand the origin of the WFM, we need to understand not only the alignment in the film, but the vector orientation of the molecular dipoles. Linear techniques, such as NEXAFS, can only determine the average alignment of molecular systems as they are only sensitive to the even moment of the orientation distribution function. Second order nonlinear techniques, such as second harmonic generation^[24] and VR-SFG^[25], are sensitive to the odd moments of the distribution function and can thus measure orientation, i.e., the total vector direction of a particular functional group. The vector nature of SFG implies that the signal is null for isotropically distributed chromophores. This makes the technique uniquely sensitive to the interfaces between centrosymmetric media (such as liquids) where symmetry is intrinsically broken. Additionally VR-SFG, as a vibrational spectroscopy, characterizes the orientation of specific functional groups in a complex molecular film. We used VR-SFG^[15] to determine the dipole orientation of SB groups in PSBMA WFM films on Au, where PSBMA reduced the WF by about 1.5 eV. For PSBMA/Au, the orientation of the SO₃⁻ groups were directed towards the substrate, i.e., on average the O atoms of the SO₃⁻ were closer to the Au surface. This supported the assignment of the PSBMA dipole directed away from the substrate (negative end nearer the Au, positive end more distant from the Au). Experimental and mathematical details related to the VR-SFG experiments are given in ref. 15.

Figure 7 shows the VR-SFG spectra of C₆₀-SB on ITO, along with that of C₆₀-SB on Au. The strong feature near 1035 cm⁻¹ is assigned to the symmetric stretch of the nominally C_{3v} SO₃⁻. In general, due to the coherent nature of the spectroscopy, a VR-SFG spectrum will be of the form:

$$Intensity \propto \left| A_{nr} + \sum \frac{A_j e^{i\phi_j}}{\nu_j - \nu_0 + i\Gamma_j} \right|^2 \quad (\text{Eq. 1})$$

where A_{nr} represents a broad-band non-resonant signal contribution, typically arising from the electronic discontinuity at the interface, and the sum is over all SFG active vibrational modes in the observed spectral region.^[26] The magnitude A_j and phase ϕ_j of the vibrational contributions reflects the 3rd rank intrinsic SFG transition tensor and the modulation of the incident and outgoing fields due to the linear optics of the thin film system (the Fresnel and local field factors). It is the interference between the non-resonant local oscillator field and the vibrationally resonant fields that enables VR-SFG to determine orientation. In general, accurate calculation of Eq. 1 is complex. However, qualitative orientation can be extracted

by simple comparison. In Figure 7, the SFG signal from the SO_3^- of C_{60} -SB exhibits *constructive* interference. Also shown in Figure 7 is the spectrum of a self-assembled monolayer (SAM) of 1-mercapto-3-isopropyl sulfonate (MPSA) on Au. It is well established that MPSA forms monolayer SAMs covalently linked to the Au through the thiol, resulting in films in which the SO_3^- points “up”, away from the Au (vector sum of the S-O directors, up, S-C director down). The orientation for the SO_3^- clearly results in a VR-SFG resonance that interferes *destructively* with the non-resonant background (NRB) of the Au, causing the resonance to show as a dip (“down peak”) in the SFG signal. As the thin film optics for the monolayer SAM and ≈ 10 nm C_{60} -SB film are similar on the scale of the coherence length, the constructive interference exhibited by C_{60} -SB/Au establishes that for C_{60} -SB/Au, the SO_3^- groups point down, towards the Au (as found for PSBMA/Au) and opposite to MPSA/Au.

To assign the orientation of C_{60} -SB on ITO in a similar fashion, we calibrated the difference between the complex A_{nr} for ITO and that for Au by comparing VR-SFG spectra for SAMs formed from para-nitrobenzenethiol (on Au), para-nitrobenzene phosphonic acid (on ITO), octadecanethiol (on Au), and octadecylphosphonic acid (ODPA, on ITO). The data is presented in the SI (Figure S4 & S5). In both the 1330 cm^{-1} region of the NO_2 symmetric stretch and the 2900 cm^{-1} region of the CH_3 stretches, the phase of the A_{nr} for ITO is nearly identical to that of Au. This is consistent with the nonlinear susceptibility being dominated by the Drude-like NIR and IR response of the conductive interfaces. Given the nearly identical A_{nr} for ITO and Au, the constructive interference in the C_{60} -SB/ITO SFG spectra implies the SO_3^- for C_{60} -SB/ITO is directed towards the surface, as for C_{60} -SB/Au and PSBMA/Au.

The NEXAFS results suggest the presence of a disordered, random free surface. At both interfaces (substrate and air) the fulleropyrrolidines may orient. Entropic free-volume considerations would favor presenting the flexible substituents outward. As the SO_3^- is at the substituent terminus, and will additionally be stabilized by image interaction on Au and possibly ionic interactions on the polar ITO, it is reasonable that the SO_3^- points down at the buried interface. If a similar orientation of the molecules was adopted at the air interface (SO_3^- pointing outwards from the film) the VR-SFG signal would be very weak due to cancellation of the two interfaces. The observation of the signal, combined with the weak NEXAFS, suggests that the air interface is disordered and the dominant origin of the signal is the buried, substrate interface. An alternative is that the SO_3^- at the air interface is “tucked in” (facing the bulk film) and thus pointing down, towards the substrate; however, the weak NEXAFS severely constrains the degree of order at the free interface.

To determine the dipole direction for C_{60} -N, two portions of the VR-SFG spectrum were characterized. First, the SFG spectra of the CH_3 methyl groups attached to the three terminal N atoms, in the region of the methyl symmetric stretch (2880 cm^{-1}), were explored. For the symmetric stretch, the vibrational dipole lies along the C_{3v} axis of the CH_3 group. The results are shown in Figure 8, where the VR-SFG spectrum of C_{60} -N is compared to a reference, an octadecane SAM on ITO ($\text{ITO-PO}_3\text{-(CH}_2\text{)}_{17}\text{-CH}_3$) prepared from ODPA. For the reference SAM, the terminal CH_3 is known to point “up”, away from the ITO. Since the

spectrum of C₆₀-N/ITO is the same as that of the ODPA/ITO, we conclude that the CH₃ groups of C₆₀-N/ITO also point “up”. This suggests that the N lone pair is toward the ITO.

Additionally, we have studied the C₆₀ modes at 1430 cm⁻¹ (F_{1u(4)} mode), and 1470 cm⁻¹ (A_{g(2)} mode) for both C₆₀-SB and C₆₀-N on ITO. Symmetry forbidden in pure C₆₀, they are prominent features in the VR-SFG spectra of substituted C₆₀ molecules. Wei *et al.* have previously studied these modes in PCBM using VR-SFG supported by DFT calculations.^[27] They identify the dipole moment of the A_{g(2)} mode as pointing from the center of C₆₀ to the functionalized position of methanofullerene. The dipole direction of the F_{1u(4)} mode is almost perpendicular to that of the A_{g(2)}. The spectra of both C₆₀-SB/ITO and C₆₀-N/ITO are shown in Figure 9. The spectra for both modifiers are extremely similar. This suggests that the orientation of the C₆₀ moiety on ITO is very similar for both C₆₀-SB and C₆₀-N. We established that for C₆₀-SB/ITO, the SO₃⁻ of the three SB zwitterionic arms pointed down towards the ITO. The similarity of the C₆₀ spectra for both C₆₀-N and C₆₀-SB suggests that the three O(CH₂)₃N(CH₃)₂ arms also point in a similar direction with the N interacting with the ITO. Thus, considering the lone pair of the amines as the key functional moiety, C₆₀-N adopts an analogous interfacial organization to that of C₆₀-SB: the electron rich portion of the substituent chain migrates to the interface, stabilized by image and possibly covalent interactions.

Shown in Figure 10 are VR-SFG from the same spectral region for C₆₀-N and C₆₀-SB on a Au substrate. The near identical character of the spectra, both in relationship to each other and in relationship with the films on ITO (Figure 9) clearly establish a common orientation of both fulleropyrrolidone species on both substrates.

The origin of action of WFM layers is complex, as the final E_F position arises from the interplay between interface dipoles due to the polarization effect between the substrate and film, molecular dipoles (if present) in the film itself, and space charge fields, as reflected in Figure 4. The observation that both C₆₀-N and C₆₀-SB lower the WF of *both* noble metals and ITO indicates that, if the dominant effect is due to molecular dipoles, the dipole must be always oriented with the negative end towards the substrate as shown in Figure 4. VR-SFG clearly establishes that this is the case for C₆₀-SB on both ITO and Au: the net orientation of SO₃⁻ is with the negatively polarized O atoms directed towards the surface (and the isopropyl chain, by implication, away). The observation of interfacially oriented amines for C₆₀-N, combined with the opposite orientation of the total fulleropyrrolidine molecular dipole (scheme 1) suggests that, for C₆₀-N, the dominate WF change is due to the interaction of the negative lone-pair with the substrate (and the subsequent alignment of the amine dipole in the opposite direction as the gas-phase structure of scheme 1). This is consistent with the DFT calculations reported for ethylamine on Au and ZnO surfaces.^[8] The >1 eV WF decrease was observed to be nominally equally shared by the orientation of the amine dipole (N “down”, alkyl “up”) and charge transfer from the N lone pair into the substrate. The similar effects of C₆₀-N and C₆₀-SB thus arise from the electron rich nature (amine, sulfonate) of the conformationally most flexible portions of the molecule, consistent with the proposal of Reenen et al., based on the similar behavior of poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN).^[28, 29]

To demonstrate improved electron injection from lowered WF and EIB, electron-only devices were fabricated with structure of Al (80 nm)/Ca (10 nm)/C₆₀ (200 nm)/(C₆₀-N or C₆₀-SB or without an EIL)/ITO. Figure 11 shows (a) the device structure and (b) the current density-voltage (J-V) characteristics. The J with C₆₀-N or C₆₀-SB interlayers is significantly improved as compared to that without an EIL. Note that, consistent with the energy level diagram of Figure 11, suggesting essentially ohmic contacts for C₆₀-N, C₆₀-N devices show a higher J than C₆₀-SB devices. The good transport through the C₆₀ layer is demonstrated by the large, compared to a tunnel junction, optimized layer thicknesses of 16 nm for C₆₀-N and 8 nm for C₆₀-SB.

In summary, the origin of WF reduction by an insertion of C₆₀-N and C₆₀-SB interlayers was investigated by probing their electronic and molecular structure on ITO. The lone pair of electrons of C₆₀-N, and ammonium and sulfonate groups of C₆₀-SB generate dipole moments. In both C₆₀-N and C₆₀-SB, the negatively polarized components of the groups are directed towards the substrate. The dipole moments induce polarization of the ITO surface leading to the formation of an interface dipole, which serves to reduce the WF. The WF of ITO was significantly reduced to 3.65 eV with C₆₀-N, and 4.05 eV with C₆₀-SB. Furthermore, the exact EIBs of C₆₀-N and C₆₀-SB from ITO were determined by E_t measurements. The EIB of C₆₀-N with ITO was negligible, and possessed a higher electron injection efficiency than C₆₀-SB having the EIB of 0.30 eV. The lower EIB of C₆₀-N may lead to better device performance than C₆₀-SB.

Experimental Section

UPS and IPES

To determine the E_t of C₆₀-N and C₆₀-SB, UPS and IPES measurements were conducted using a SPECS PHOIBOS 150 hemispherical analyzer and a PSP photon detector (isochromat mode, band pass filter = 9.5 eV) on the 16 nm-thick films. An ultraviolet (He I, 21.22 eV) light source and a low energy electron gun were used.^[30] Both spectrometers were calibrated with respect to the Au Fermi step as a reference and the spectral broadness of UPS and IPES was 0.1 and 0.4 eV, respectively. Nominal precision of all reported energies is ± 0.05 eV. The base pressure of the analysis chamber was maintained below 6.0×10^{-10} mbar. To reduce possible sample damage by electron beam, the electron dose was carefully controlled (sample current < 1 μ A) during IPES measurements. For thickness-dependent energy level alignment, UPS measurements were carried out using an Omicron SPHERA hemispherical analyzer and a He I light source. The fulleropyrrolidine films were spin-coated on ITO from various solution concentrations (0.06–4.0 mg/mL) at 500 rpm for 5 s and 4000 rpm for 55 s. The fulleropyrrolidine solutions in 2,2,2-trifluoroethanol (TFE) were stirred overnight at room temperature and filtered through a polytetrafluoroethylene (PTFE) membrane (0.2 μ m VWR) prior to deposition. The thicknesses were confirmed by ellipsometry.

DFT calculations

To estimate the dipole moment of C₆₀-N and C₆₀-SB, DFT calculations on a single molecule C₆₀-N and C₆₀-SB were conducted with a Becke three-parameter exchange and Lee-Yang-

Parr correlation (B3LYP) hybrid functional and a 6–31G(d,p) basis set which are implemented in GAUSSIAN 09.^[31–33] The dipole moment was evaluated at the fully relaxed geometry. Energetic minima were ensured by vibrational frequency analysis.

NEXAFS

NEXAFS spectroscopy was performed at the soft X-ray beamline at the Australian Synchrotron^[34] using a nearly perfectly linearly polarized X-ray beam. A fresh spot was used for each measurement to avoid beam damage. TEY data (presented here) was acquired by measuring the drain current flowing to the sample under X-ray illumination. Partial electron yield data was also acquired using a channeltron detector with a retarding voltage of 210 V and found to be consistent with the TEY data (not shown). The recorded signal was normalized by the “stable monitor method”,^[35] with the spectra normalized by setting the pre-edge to 0 and the intensity at 320 eV to 1.

VR-SFG

VR-SFG spectra were acquired with a custom built, broad bandwidth system. In brief, a Ti-sapphire regenerative amplifier system, generating 12 W of nominally 100 fs duration pulses at 3 kHz repetition rate was used to simultaneously pump two optical parametric amplifier (OPA) systems. In one system, a near IR OPA generated sub 100 fs pulses at $\approx(1470$ and $1750)$ nm that were sent to a non-collinear difference frequency generator to produce ≈ 5 uJ, ≈ 150 cm^{-1} bandwidth, IR pulses centered at ≈ 1100 cm^{-1} . The signal (≈ 1470 nm) and idler (≈ 1750 nm) pulses are wavelength tunable, so the IR pulses may be tuned from 600 to 4000 cm^{-1} . In the second system, a second harmonic bandwidth compressor was used to produce ≈ 3 cm^{-1} , 400 nm center wavelength pulses that pumped an OPA resulting in tunable 8 cm^{-1} bandwidth pulses centered at 785 nm. Either SSP (s-polarized sum frequency, s-polarized 785 nm, p-polarized IR) or PPP (p-polarized sum frequency, p-polarized 785 nm, p-polarized IR) SFG spectra were acquired with the 785 nm and IR incident on the sample at 35.8° and 54.2° from the surface normal respectively. The Vis pulse was delayed in time by various amounts with respect to the IR pulse, to maximize the heterodyne between the substrate and the film and minimize artifacts in the collection of the free induction decay. The sample signal was normalized to the signal from an appropriate reference: for films on ITO, a freshly UVO cleaned ITO film, for films on a Au substrate, freshly cleaned Au.

Electron-only device fabrication

ITO substrates were cleaned by ultrasonication in deionized water, detergent, acetone, 2-propanol, ethanol and deionized water again for 10 min each. After that, UV-ozone treatment was conducted on ITO for 15 min. A C_{60} electron transport layer (200 nm, Puyang Huicheng Chemical Co., purity 99%) and a Ca (10 nm)/Al (80) nm bilayer cathode were sequentially deposited with thermal evaporation at a rate of 0.01 nm/s in the high vacuum chamber below 5×10^{-6} mbar. To improve crystallinity of a C_{60} layer, the samples were annealed for 15 min at 100 $^\circ\text{C}$ under N_2 atmosphere. J-V characteristics were measured with a Keithley 4200-SCS parameter analyzer.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. UPS and IPES spectra of (a) C₆₀-N and (b) C₆₀-SB films (16 nm) for determining the E_t . The molecular structure is also shown.

Figure 2.

UPS spectra of (a) SEC region and (b) HOMO region of C₆₀-N (0.5, 1, 2, 4, 8, 12 and 16) nm films on ITO.

Figure 3.

UPS spectra of (a) SEC region and (b) HOMO region of C₆₀-SB (0.5, 1, 2, 4, 8, 12 and 16) nm films on ITO.

Figure 4.

Energy level diagram of (a) C₆₀-N on ITO and (b) C₆₀-SB on ITO (unit: eV). Ψ_{ITO} is the work function of ITO, Φ_h and Φ_e is the hole and electron injection barrier, E_{vac} is the vacuum energy level, eD is the interface dipole. The schematic illustrations display orientation of dipole necessary to achieve observed eD .

Figure 5. Optimized structure and charge distribution of (a) C₆₀-N and (b) C₆₀-SB from DFT calculations. The dipole moments were also indicated.

Figure 6. C-edge NEXAFS spectra of (a) C₆₀-N and (b) C₆₀-SB as a function of angle-of-incidence with respect to the surface plane of the incident, polarized, X-ray beam.

Figure 7.

VR-SFG spectra of a self-assembled monolayer (SAM) of 1-mercapto-3-isopropyl sulfonate (MPSA) on Au (MPSA/Au), black; a film of C₆₀-SB on Au (C₆₀-SB/Au), blue; a film of C₆₀-SB on ITO (C₆₀-SB/ITO), red. The vibrational resonance is associated with the SO₃ symmetric stretch. Polarization is ppp. Time delay between IR and Vis pulses is 0, 0.67 ps and 2.0 ps, respectively. C₆₀-SB/ITO, right axis; Modifiers on Au, left axis

Figure 8. VR-SFG spectra of an octadecane SAM on ITO prepared from octadecylphosphonic acid (ODPA/ITO), blue, and a film of C₆₀-N on ITO (C₆₀-N/ITO), red. Vibrational resonances are associated with the terminal methyl CH₃ groups. Polarization is ppp, IR-Vis delay time is 2.0 ps.

Figure 9. VR-SFG spectra of films of C₆₀-N on ITO (red) and C₆₀-SB on ITO (blue). Polarization is ssp; IR-Vis delay time is 1.33 ps.

Figure 10. VR-SFG spectra of films of C₆₀-N on Au (red) and C₆₀-SB on Au (blue). Polarization is ssp; IR-Vis delay time is 0 ps. C₆₀-N plotted on left axis, C₆₀-SB on right.

Figure 11.

Device structure and J-V characteristics of electron-only devices with a C_{60} -N or C_{60} -SB or no EIL.

Scheme 1.
Structure of C₆₀-N and C₆₀-SB.

Table 1

Summary of NEXAFS dispersion parameters

	ITO		Au	
D^a	< 289 eV mostly π^*	> 289 eV mostly σ^*	< 289 eV mostly π^*	> 289 eV mostly σ^*
C60-N	0.03	0.04	0.04	0.08
C60-SB	0.10	0.04	0.05	0.08

^atypical uncertainty +/-0.01 from the linear fit extrapolation to end points.