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Electronic Structure of Fullerene Acceptors in Organic Bulk-Heterojunctions: A Combined EPR and DFT Study

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Abstract

Organic photovoltaic (OPV) devices are a promising alternative energy source. Attempts to improve their performance have focused on the optimization of the electron-donating polymers, while electron-accepting fullerenes have received less attention. Here, we report an electronic structure study of the widely used soluble fullerene derivatives PC₆₁BM and PC₇₁BM in their singly reduced state, that are generated in the polymer:fullerene blends upon light-induced charge separation. Density Functional Theory (DFT) calculations characterize the electronic structures of the fullerene anions through spin density distributions and magnetic resonance parameters. The good agreement of the calculated magnetic resonance parameters with those determined experimentally by advanced EPR spectroscopy allows the validation of the DFT calculations. Thus, for the first time the directions of the main g-tensors axis were determined in the molecular frame. For both systems, no spin density is present on the PCBM side chain and the axis of the largest g-value lies along the PCBM molecular axis. While the spin density distribution is largely uniform for PC₆₁BM, it is not evenly distributed for PC₇₁BM.

INTRODUCTION

Global energy demands are predicted to increase by 35% in the next 25 years.¹ For various reasons, this demand cannot continue to be met by relying to a large part on fossil fuels.² The best way to overcome the global dependence on fossil fuels is to switch to renewable energy sources such as sunlight, wind, water, biomass, and geothermal.^{2, 3} Comparative analysis shows that potentially the most promising, clean and sustainable resource is solar energy.^{4–6} There are number of ways to utilize and harvest solar energy. The most common are known as solar-to-fuel and solar-to-electricity approaches.^{6, 7} In the former case, solar energy is transformed and stored in the energy of chemical bonds of the fuel, while in the latter case solar energy is stored as electrical potential of separated charges by utilizing photovoltaic (PV) solar cells. Currently, industrial energy production almost exclusively uses silicon based PV devices. The organic PVs (OPV) and hybrid PVs, such as recently emerging perovskite PVs, are still a field of extensive research and development.^{8–11} OPV devices are already in use in applications which have special demands like light weight and

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transportability, where those devices have distinct advantages over conventional PV devices.¹²

The initial discovery of charge transfer in polymer-fullerene systems, and thus their possibilities as organic photovoltaic cell materials was made in 1992.¹³ While at first device efficiencies were very low, they are now generally between 8–9% with a recent report of 10.7%.^{14–15} Upon light excitation, the neutral excitons break down into two spin-carrying charged counterparts, the positive and negative polaron on the polymer and the fullerene, respectively.^{8, 16} Using the chemical/molecular terms instead of the solid state physics terms, light irradiation creates excited singlet states which subsequently decay via charge transfer to radical cations and radical anions. Since the organic bulk-heterojunctions (BHJ) under investigation lack the characteristics of distinctive semiconductors, but have the characteristics of typical molecular systems, the use of the chemical terms seems more appropriate and is used in the following.

Much recent research has focused on the improvement of the polymer-donor materials resulting in the design of number of novel low band gap polymers.^{8, 17, 18} Most of the novel polymers and their corresponding radical cations have been well characterized spectroscopically and computational approaches have been used to model experimental data and their electronic structure.^{8, 16, 19} However, other than the invention of the soluble derivatives of C₆₀ and C₇₀ (termed PC₆₁BM and PC₇₁BM, respectively),^{20,21} changes to the electron acceptors have not resulted in significant improvements to the efficiencies. Furthermore, the computational treatment of the fullerenes remains a challenge due to their complex electronic structure with large numbers of degenerate, or close to degenerate states.

To reveal the electronic structures of the light-induced anion radicals localized on the fullerene derivatives, PC₆₁BM and PC₇₁BM, in the polymer-fullerene OPV active blends, we have used advanced EPR spectroscopy combined with Density Functional Theory (DFT) calculations. These two fullerene derivatives are the most widely used ones in OPV materials. Their structures are shown in Scheme 1.

The radical anions of the fullerene derivatives were created at low temperature by *in situ* illumination of corresponding BHJ fullerene:polymer blends in the resonator of the EPR spectrometer. P3HT was used as the polymer component in the blends, since it has been used in many previous studies and is well characterized. EPR spectra, which are the “spin signature” of the radical’s electronic state, were recorded by conventional X-band EPR and by high frequency D-band EPR spectroscopy. While conventional X-band (9–10 GHz) EPR spectroscopy allows one to largely separate the signals of anion and cation radicals on PC₆₁BM and P3HT, their g-tensors are not fully resolved. In the case of the PC₇₁BM:P3HT blend the EPR signals of negative and positive radicals are strongly overlapped at X-band (Figure 1). These problems were addressed by using high frequency D-band (130 GHz), which has 14 times greater g-tensor resolution compared to conventional X-band. Computer simulation of the spectra yielded magnetic resonance parameters as shown in Table 1. The D-band EPR spectra of both fullerene radical anions demonstrate almost axial symmetry of the g-tensors with very broad parallel components. However, there is a striking difference between the EPR “spin signatures” of anion radicals (negative polarons) in PC₆₁BM and

PC₇₁BM, namely, the unexpected shift of the g-values of the PC₇₁BM anions compared to the PC₆₁BM anions. In particular, as shown in Figure 1 and Table 1, all three PC₆₁BM g-values are less than the free electron g-value, g_e , similar to that of shallow-trapped electrons in semiconducting materials,^{22, 23} while the PC₇₁BM g-values are around or greater than g_e , which is typical for shallow-trapped donors in semiconductors²⁴ or pure organic radicals.^{25–27}

Although the difference in g-values between PC₆₁BM and PC₇₁BM radical anions has been reported before,^{28–31} a satisfactory explanation for this striking deviation has not been presented. For fullerenes in general, these shifts have been tentatively attributed to the spin-orbit interaction on a distorted fullerene cage,¹³ to the static Jahn-Teller effect,^{32, 33} or to differences in the Jahn-Teller dynamics for C₆₀ and C₇₀ molecules.³² Moreover it is not clear why, in spite of the high symmetry of the fullerene molecule, the g-tensor of PC₆₁BM as well as PC₇₁BM anion is anisotropic. Currently, there is no unified theory that can explain g-tensors of both C₆₀^{•−} and C₇₀^{•−} radicals. To address these questions we use DFT modeling to calculate the electronic structure and combine this with experimental EPR data to verify the validity of the theoretical approach. We have recently shown that this type of approach can be successfully applied to OPV materials.^{31, 34–36}

As shown in Table 1, there is a good agreement between experimental and calculated values of the g-tensor for the PC₆₁BM anion. Note, that we listed the g-values as $g_3 > g_2 > g_1$, where g_1 , g_2 , and g_3 are the principal axis components of the g-tensor. The values for g_2 and g_3 are nearly identical while g_1 is much smaller. This is in contrast to PC₇₁BM, where both calculated and experimental values of g_1 and g_2 are similar in magnitude and the largest g value (g_3) stands out. Evaluating the precise agreement between experimental and calculated values for the PC₇₁BM anion is complicated as the symmetry of C₇₀ allows three possible isomers when the PCBM side chain is attached (Scheme 1).²¹ While it is generally accepted that the synthesized molecule exists in a roughly 85/15 split between the α and two β isomers, the precise isomer ratio may depend upon particular synthetic pathway and purification procedure. According to our DFT calculations, all isomers have slightly different g-values (Table 1), and the difference in resonance field is comparable in magnitude to the line broadening in D-band EPR spectra. This makes direct comparison of theoretical and experimental data less straightforward. Weighted average values of the calculated g-tensor components (shown in Table 1) demonstrate a reasonable agreement with the experiment. For PC₆₁Bm and a-PC₇₁BM, the calculated g-values were essentially unchanged by the choice of various basis sets for both the optimization and the EPR calculations, while for the two β -isomers of PC₇₁BM a very weak dependence on the basis set was found. (see Supporting Information Tables S1-S2).

Note that the calculations somewhat underestimate the g-tensor anisotropy ($g_3 - g_1$ difference) for the PC₇₁BM case although agreement is still good. Previously we reported a solution dependent shift of the g_3 as well as strain effect on the g_3 -component of the same order of magnitude, < 0.001 .³¹ For organic radicals, a shift of this size may be due to environmental effects, when a large fraction of spin density is localized on atoms with large spin-orbit coupling, such as oxygen (or nitrogen). In these cases, the solvent is very often engaged in direct hydrogen bonding with the oxygen (or nitrogen).^{37–39} However, as shown

below, the fullerenes under study have two oxygen atoms with large spin orbit coupling constants but insignificant spin density on these oxygen atoms. Moreover, the unpaired electron is strongly delocalized over the fullerene cage, which makes an effect of specific interaction negligible. We observed that g-strain depends not only upon the solvent but also upon sample preparation: freezing and annealing protocol, i.e. nonspecific interaction with an environment. Based on these data we tentatively attribute g-strain and g-shift of the parallel components in PC₆₁BM (g_1) and PC₇₁BM (g_3) anions to the mechanical deformation of the fullerene cages by the solid environment which exerts pressure on the fullerene molecule in films or frozen solutions.

In order to better understand and visualize the differences in the electronic structures between PC₆₁BM and PC₇₁BM radical anions, we used DFT to calculate the spin density distribution (Figure 2). For all four fullerenes, virtually no spin density is found on the side chain; for PC₆₁BM less than 0.2% of the unpaired spin density is present on the side chain; for α -PC₇₁BM, less than 0.3% on the side chain. The calculated electron hyperfine coupling with the side chain protons is less than 0.5 MHz, which is similar to the pure dipole electron-nuclear interactions with matrix (distant) protons and in excellent agreement with the ENDOR data reported for the PC₆₁BM radical anion.³¹

While the g-tensor axes shown in Figure 2 vary between PC₆₁BM and PC₇₁BM radical anions, the axis of the largest g-value (g_3) is always aligned with the principal axis of the fullerene cage: this is the elongation axis for PC₇₁BM and the axis connecting the center of the fullerene and cyclopropyl ring of side chain for PC₆₁BM. This results in alignment of the principal molecular axis and the largest g-tensor axis (g_3) for PC₆₁BM and the α -isomer of PC₇₁BM. In contrast, for the two β -isomers of PC₇₁BM, where the side chain is bound to a less polar bond^{21, 40} off center of the long axis of the C₇₀ cage (see Scheme 1), the largest g-value remains aligned with the fullerene main axis, and is skewed with respect to the side chain. Note, that for PC₆₁BM the g_1 component and for all three PC₇₁BM isomers the g_2 components are in the plane of the cyclopropyl ring. This suggests that even though the side chain carries essentially no spin density, its addition and resulting symmetry breaking of the fullerene cage contributes to the g-tensor anisotropy.

An important finding is that the spin localization pattern on the fullerene cage exhibits noticeable differences between the PC₆₁BM and PC₇₁BM radical anions. For PC₆₁BM the spin density is delocalized broadly in a kind of “belt” around the entire molecule, while for the PC₇₁BM molecules, the spin density is localized on one side of the molecule (Figure 2); this is most visible for the α -isomer. The difference in spin density delocalization is reproduced in calculations with different basis sets (SI Table S2). While it has been suggested that the B3LYP functional is non-ideal for the calculation of spin properties due to errors in its treatment of correlation effects,⁴¹ the non-symmetric delocalization in spin density persists for all functionals used in our calculations with different inclusion of correlation (SI Table S3). Furthermore, the agreement between g-values calculated using different functionals and basis sets and experimental g-values supports our spin density calculations. Despite the different locations of spin density, both PC₆₁BM and PC₇₁BM have approximately the same percentage of carbons with very small and very large spin populations (see SI Table S6-S7 and Figure S2). Therefore, the primary difference between

PC₆₁BM and PC₇₁BM radical anions is the spin density delocalization pattern. We propose that the observed difference in delocalization pattern is responsible for the shift of the g-values of PC₇₁BM compared to PC₆₁BM.

To summarize, we have carried out a comprehensive EPR and DFT study of the characteristic EPR signals of the fullerene anion radicals in polymer-fullerene BHJ blends. EPR spectroscopy reveals a striking difference in the g-values of anion radicals in PC₆₁BM compared to PC₇₁BM in BHJ blends. This difference was correctly reproduced by DFT calculations which demonstrate that almost no spin density is present on the PCBM side chain. Furthermore, the three PC₇₁BM structures have spin density localization patterns that are not symmetric with respect to the molecule while the PC₆₁BM spin density contours ring the entire molecule. We propose that this difference in spin density pattern correlates with the different shifts of the g-values of PC₆₁BM and PC₇₁BM with respect to the free electron g-value, g_e . We also tentatively assign the pronounced g-strain effect in the parallel components of the fullerene anion g-tensors to the mechanical interactions of the flexible fullerene cage with the heterogeneous environment of BHJ. The largest g tensor axis lies along the long axis of the fullerene cage for PC₇₁BM irrespective of the location of the side chain, and along the axis connecting center of the fullerene and cyclopropyl ring of side chain for PC₆₁BM. This work clearly demonstrates that advanced EPR spectroscopy in combination with DFT is an extremely powerful approach for investigation of the electronic structure of the charge separated states in organic photovoltaic materials.

EXPERIMENTAL AND COMPUTATIONAL METHODS

EPR Spectroscopy

Continuous wave (cw) X-band (9–10 GHz) EPR experiments were carried out with a Bruker ELEXSYS E580 EPR spectrometer (Bruker Biospin, Rheinstetten, Germany), equipped with a Flexline dielectric ring resonator and a helium gas-flow cryostat (CF935, Oxford Instruments, UK). Light excitation was done directly in the resonator with 532 nm Laser light (Nd:YAG Laser with OPO, model Vibrant from Opotek) or a 300 W Xenon lamp (LX 300F from Atlas Specialty Lighting). When using the lamp, a water filter (20 cm pathlength) was used to avoid unwanted heating of the sample. In addition, a KG3 short pass filter (Schott) removed residual IR irradiation. In both setups (Laser and lamp), a GG400 long pass filter (Schott) was used to remove UV light. Typical incident light intensities at the sample were around 2 W for the lamp and 40 mW for the Laser. High frequency (HF) EPR measurements were performed on a home-built D-band (130 GHz) spectrometer equipped with a single mode TE₀₁₁ cylindrical cavity.^{42, 43} EPR spectra of the samples were recorded in pulse mode in order to remove the microwave phase distortion due to fast-passage effects at low temperatures. Light excitation was done directly in the cavity of the spectrometer with 532 nm Laser light through an optical fiber (Nd:YAG Laser, INDI, Newport). Data processing was done using Xepr (Bruker BioSpin, Rheinstetten) and MatlabTM 7.11.1 (MathWorks, Natick) environment. Simulations of the EPR spectra were performed using the EasySpin software package (version 4.0.0).⁴⁴

Density Functional Theory (DFT) Calculations

Initial fullerene structures were constructed from available C₆₀⁴⁵ and C₇₀⁴⁶ model compounds and pre-built and optimized PCBM fragments. The geometry optimizations were carried out using density functional theory (DFT) and the B3LYP functional^{47–50} using, successively, the 3–21G, 6–31G, and the 6–31G+(d) basis set, as implemented in PQSMol.⁵¹ Frequency calculations were performed on all optimized structures to ensure stable minima were obtained. The spectroscopic parameters were obtained via single point DFT calculations, performed with the program package ORCA (v 2.9.1)⁵² with the B3LYP functional in combination with the EPRII basis set.^{53, 54} To test the influence of the basis set on the calculated EPR parameters, additional single point calculations using the same geometry (optimized at 6–31G+(d) basis containing both diffuse and polarized terms) and the def2-TZVPP basis set of Ahlrich's and co-workers^{55–57} were performed and compared to the EPRII results. The principal g-values were calculated employing the coupled-perturbed Kohn-Sham equations and the spin orbit operator computed using the RI approximation for the Coulombic term and the one-center approximation for the exchange term (RIJCOSX SOMF(1X)).⁵⁸ The anisotropic magnetic dipole and the isotropic Fermi contact contributions to the hf-coupling were calculated for all ¹H and ¹³C atoms. To determine the effect of the basis set used in optimization, all structures were optimized *in vacuo* using 3–21G, 6–31G, and 6–31G+(d) basis sets, using successively, the 3–21G, 6–31G, and the 6–31G+(d) basis sets. In general, increasing the basis set had little effect on the structure with RMSD values for the fullerene itself around 0.01 Å between the 6–31G and the 6–31G+(d) and around 0.1 Å between the 3–21G and the 6–31G+(d) basis sets. Calculation of the EPR g values for each structure gave very similar results (see Supporting Information, Table S1). Furthermore, the EPR parameters calculated using the EPRII basis set are very similar to those calculated using the larger def2-TZVPP basis set (see Supporting Information, Table S2). Finally, to assess the robustness of the results with respect to functional choice, the g-values were calculated using a variety of functionals (see Supporting Information, Table S3). Atomic coordinates for all structures at the 6–31G+(d) level are given in the supporting information (Tables S3–S6).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

EPR spectra of PC₆₁BM and PC₇₁BM radical anions at X-band (9–10 GHz) and D-band (130 GHz). The fullerene radical anions have been created by light-induced electron transfer in the BHJ blends (with P3HT) at low temperature. Continuous wave (CW) X-band EPR spectra were recorded as first derivatives of the absorption, while pulsed D-band EPR spectra were recorded as absorption. Experimental traces are in black, computer simulations of the fullerene radical anions in red, computer simulations of P3HT radical cations in green, sum of computer simulations in blue. Simulation parameters are summarized in Table 1.

Figure 2. Spin density iso-surface plots of the optimized lowest energy conformation at 6-31G+(d) using the B3LYP functional for each of the fullerenes studied. All iso-surfaces are shown at a contour level of 0.001 e/a_0^3 . The second row shows orientations rotated 90 degrees with respect to the first row. Arrows show the orientation of the g-tensors.

Scheme 1.

Structures of the C₆₀- and C₇₀-derivatives: [6,6]-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM) and isomers of [6,6]-phenyl C₇₁ butyric acid methyl esters (PC₇₁BM).^{20, 21} All three PC₇₁BM isomers are shown in the same orientation to aid in the visualization of the PCBM side chain location. Red color indicates the position of oxygen atoms.

Table 1

The principal values of the g-tensors of anion radicals of the fullerenes as determined experimentally in frozen toluene solution of P3HT:fullerene blends and calculated using the EPRII basis set and B3LYP functional for the structures optimized at the 6-31G+(d)B3LYP level (see Methods section for details). The large distribution of the parallel component of the fullerene g-tensor induces an error of 0.0003 in the experimental values. Numbering of the g-values follows the scheme employed by the ORCA program package, $g_3 > g_2 > g_1$.

g	$PC_{60}BM^{\cdot-}$		α $PC_{71}BM^{\cdot-}$		$\beta_1 PC_{71}BM^{\cdot-}$		$\beta_2 PC_{71}BM^{\cdot-}$		$PC_{71}BM^{\cdot-}$	
	Calculated	Experimental	Calculated	Calculated	Calculated	Calculated	Avg*	Experimental		
g_3	2.0009	2.0006	2.0054	2.0048	2.0047	2.0053	2.0053	2.0060		
g_2	2.0008	2.0005	2.0035	2.0029	2.0029	2.0034	2.0034	2.0028		
g_1	1.9995	1.9985	2.0026	2.0019	2.0017	2.0025	2.0025	2.0021		

* Calculated values are averaged 85% α ; 15% β_1 and β_2 . These values follow the distribution of isomers reported in 21