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The first phosphorus-containing fullerene derivative applied as an electron acceptor material in organic solar cells

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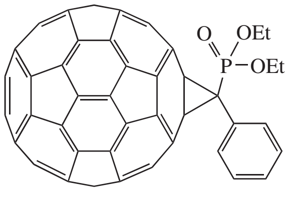
A phosphorus-containing fullerene derivative was successfully applied as an electron acceptor material in organic solar cells with power conversion efficiencies comparable to the values obtained using the state-of-the-art P3HT/PCBM composite system.

Extensive research in the field of organic solar cells during the last decade resulted in a gradual increase in power conversion efficiencies from relatively low values of ~1% up to appreciably high 5–6%, as reported recently.[1–4] The design of photoactive conjugated polymers and fullerene derivatives is of considerable current interest.[5,6] The range of fullerene derivatives that are promising materials for organic solar cells is very limited. These are few methanofullerenes bearing aliphatic and aromatic (phenyl, thienyl) substituents together with a couple of fullerene derivatives with fused cyclohexane moieties.[7–11] All of these compounds contain carbon, hydrogen, oxygen and scarcely sulfur in their molecular frameworks. We believe that the presence of elements such as silicon or phosphorus can improve the electronic properties and environmental stability of the materials. This hypothesis was proved for electron donor conjugated polymers.[12]

Here, we demonstrated for the first time that phosphorus-containing fullerene derivatives have large potential to be applied as advanced electron acceptor materials for organic photovoltaics. Compound **1** is the phenyl-C_{61}-phosphonic acid diethyl ester (PCPDE) according to the nomenclature commonly accepted for conventional fullerene-based compounds. For instance, a short name of the well-known material PCBM (**2**) was formed from its full name, phenyl-C_{61}-butyric acid methyl ester (Figure 1).[13]

PCPDE was synthesized earlier,[14] and it was noticed that the electrochemical reduction of PCPDE is fully reversible at least with the formation of mono- and dianions. On the contrary, all other known phosphorylated fullerene derivatives rapidly undergo the retro-Bingel reaction upon acceptance of the second electron.[15]



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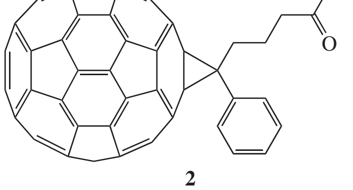

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Figure 1 Molecular structures of PCPDE **1** and PCBM **2**.

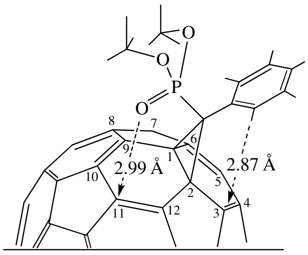

Figure 2 The most thermodynamically favourable conformation of the organic addend in PCPDE according to the DFT calculations.

On the basis of the ^{1}H and ^{13}C NMR spectral data and theoretical calculations, it was suggested that the stability of PCPDE is directly related to strong electronic interactions between the phosphonic acid fragment and the fullerene cage.[14] DFT calculations suggested that an oxygen atom can approach the C(11)–C(12) double bond of the fullerene cage by 2.99 Å, while a hydrogen atom at the *ortho*-position of the phenyl ring can come closer to the C(3)–C(4) double bond by 2.87 Å (Figure 2).[14] Note that the conformation of the phosphoryl group and the internuclear distances O···C and H···C remain in the radical-anion. Similar results were reported for another type of fullerene derivatives, where the intramolecular O···H and N···H hydrogen bonds strongly stabilized the entire molecule and significantly affected its electrochemical behaviour.[16]

We performed the X-ray single crystal structure determination for PCPDE.[†] In the crystal, the molecule of PCPDE has a short intramolecular contact between the oxygen atom [O(61)] and a carbon atom of the fullerene sphere [C(11)]. The distance between O(61) and C(11) is 2.942(5) Å, which is shorter than the sum of their van der Waals radii by 0.28 Å (Figure 3).

The observed electronic interaction between the oxygen atom of the phosphonic ester moiety and the fullerene cage can influence significantly the electronic properties of PCPDE. It is well known that the electronic properties of materials govern photoinduced charge separation in the active layer of an organic solar cell and define the maximum open-circuit voltage of the device (V_{oc}). Usually, it is estimated as energy difference between

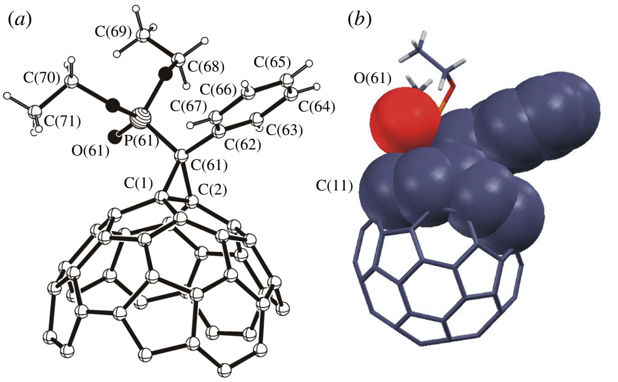

Figure 3 (*a*) Fragment of the molecule of PCPDE as determined from the X-ray single crystal diffraction data. (*b*) Illustration of the short O(61)···C(11) intramolecular contact using spheres for the representation of van der Waals radii of some atoms. Solvate chloroform molecules are omitted for clarity.

the HOMO level of the donor and the LUMO level of the acceptor materials minus 0.3 V, which is an empirical constant accounting for typical potential loss at the active layer/electrode interfaces:[17]

$$V_{\mathrm{oc}}^{\mathrm{max}} = E_{\mathrm{LUMO\text{–}acceptor}} - E_{\mathrm{HOMO\text{–}donor}} - 0.3\ \mathrm{V}.$$

Therefore, we performed DFT calculations to determine the energy levels of PCPDE, C_{60} and PCBM and to reveal which of these compounds has optimal electronic properties for applications in organic solar cells. Indeed, the calculated LUMO energy of PCPDE was about 0.09 and 0.26 eV higher than the LUMO energies of PCBM and C_{60}, respectively. Therefore, PCPDE should give ~90 mV higher V_{oc} than the state-of-the-art photovoltaic material PCBM. Thus, theoretical calculations undoubtedly suggested that PCPDE is a very promising material for organic solar cells.

Table 1 Energy levels of C_{60}, PCBM and PCPDE and estimated V_{oc} values for solar cells based on their composites with P3HT.[a]

Compound	DFT			CV		
	LUMO/eV	HOMO/eV	V_{oc}/V	$E_1^{1/2}$/V *vs.* Fc/Fc$^+$	LUMO/eV	V_{oc}/V
C_{60}	–4.38	–6.02	0.83	–1.03	–3.77	1.03
PCBM	–4.21	–5.68	1.00	–1.13	–3.67	1.13
PCPDE	–4.12	–5.58	1.09	–1.13	–3.67	1.13

[a] $E_1^{1/2}$ – the first half-wave reduction potential of the compound; V_{oc} was estimated using given above equation and *E*(HOMO-P3HT) = –5.1 eV according to ref. 17.

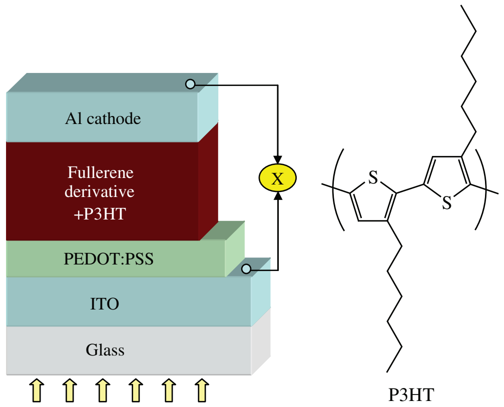

Figure 4 Schematic diagram of the photovoltaic cell (left) and molecular structure of the regioregular P3HT (right).

Table 2 Output parameters of organic solar cells comprising PCPDE or PCBM in photoactive layers.

Composite (conditions)	I_{sc}/mA cm^{-2}	V_{oc}/mV	FF (%)	η (%)
PCPDE/P3HT (as prepared)	7.6	600	35	1.60
PCPDE/P3HT (annealed at 155 °C for 3 min)	4.0	550	47	1.04
PCBM/P3HT (annealed at 155 oC for 3 min)	7.0	580	58	2.38

Meantime, the experimental reduction potentials of PCBM and PCPDE[14] found using cyclic voltammetry (CV) were almost identical and resulted in the same estimated LUMO energies for both compounds.[18] On the basis of these electrochemical data, similar values of V_{oc} should be expected for solar cells comprising PCBM or PCPDE as photoactive materials. Therefore, there is some discrepancy between DFT calculations and electrochemistry measurements performed for PCPDE.

At the next step, we evaluated PCPDE as an electron acceptor material for bulk heterojunction organic solar cells. For this purpose, PCPDE (8 mg) was blended with the electron donor polymer P3HT [poly(3-hexylthiophene)] (10 mg) in chloroform (1 ml) and then spin-coated on the ITO slides covered with a PEDOT-PSS layer. The resulting 75–85 nm thick films were immediately transferred to a glove box with an inert atmosphere and dried. Then, an aluminum cathode was deposited by thermal vacuum evaporation (~100 nm). The resulting devices were sealed between two glass plates to protect them from the action of oxygen and moisture outside the glove box.

The *I–V* curves were measured for the fabricated devices in the dark and under irradiation with simulated solar light provided

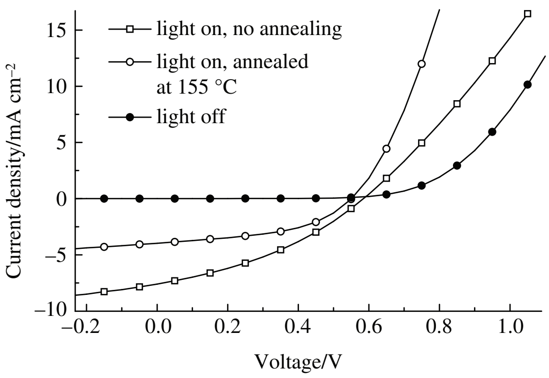

Figure 5 Light on and light off *I–V* curves for as-prepared and annealed solar cells based on the PCPDE/P3HT composite.

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† *X-ray diffraction data*. The sample of phenyl-C_{61}-phosphonic acid diethyl ester was crystallized from a mixture of CS_2 and $CHCl_3$, $C_{71}H_{15}O_3P{\cdot}CHCl_3$, $M = 1066.17$, monoclinic, space group $P2_1/c$, $a = 10.0681(9)$, $b = 24.078(2)$ and $c = 17.973(2)$ Å, $\beta = 101.407(4)°$, $V = 4270.9(7)$ Å^3, $Z = 4$, $d_{\mathrm{calc}} = 1.658$ g cm^{-3}, μ(CuKα) = 28.09 cm^{-1}, $F(000) = 2152$, 35980 reflections measured, 6872 unique ($R_{\mathrm{int}} = 0.0470$), restraints/parameters = 1/696. Final indices $R_1(F) = 0.0806$, $wR_2(F^2) = 0.2285$ for 5893 reflections with $I > 2\sigma(I)$. Goodness-of-fit on F^2 was 1.045, the largest difference peak and hole are 1.029 and –0.986 eÅ^{-3}, respectively. Cell parameters and intensities for single crystals were measured at 296 K on a Bruker AXS Kappa Apex diffractometer using CuKα radiation with a graphite monochromator. Data were corrected for the absorption effect using the SADABS[22] program. The structure was solved by a direct method and refined by the full matrix least-squares using the SHELXTL[23] and WinGX[24] programs. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were located from the Fourier electron density synthesis and included in the refinement in the isotropic riding model approximation. Data collections: images were indexed, integrated and scaled using the APEX[25] data reduction package. All figures were made using the PLATON program.[26]

CCDC 747602 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2010.

by a KHS Steuernagel solar simulator calibrated to correspond to 100 mW cm^{-2} at AM1.5. First, the clear photovoltaic effect can be noticed for solar cells comprising the PCPDE/P3HT composite. Appreciably high short circuit current (I_{sc}) densities of 7.6 mA cm^{-2} and V_{oc} of 600 mV were obtained together with a disappointedly low fill factor (FF) of only 35%. The overall power conversion efficiency (η) of solar cells was calculated using the following equation:

$$\eta = I_{sc}V_{oc}FF/P_{light},$$

where P_{light} is the power of the light beam coming from the solar simulator with AM1.5 irradiation spectrum. In our case, the light power was adjusted to 100 mW cm^{-2} (standard measurement conditions).

The calculated value of η for the PCPDE/P3HT solar cells was 1.6%. The reference PCBM/P3HT devices yielded $\eta = 2.38\%$ due to higher I_{SC} and FF values. We note that V_{oc} of the PCBM-based solar cells was ~20 mV lower than V_{OC} of the devices comprising PCPDE as an acceptor material. The DFT calculations gave a much higher difference of 90 mV between the open circuit voltages of solar cells containing PCBM or PCPDE. Therefore, the experimental results are consistent with the electrochemistry data that suggested similar V_{oc} values for both PCBM and PCPDE.

The thermal treatment of P3HT/PCBM films usually improves their photovoltaic performance.[19] However, it was opposite for PCPDE/P3HT composites. Indeed, annealing at 155 °C for 3 min improved the fill factor (up to 47%), while I_{sc} and V_{oc} dropped significantly resulting in an overall power conversion efficiency of 1.04%. Heating leads to large-scale phase separation between donor and acceptor materials as it can be deduced from the AFM image of the annealed PCPDE/P3HT composite (Figure 6). Large bright regions clearly visible in the image most likely correspond to the clusters of the fullerene derivative segregated from the polymer. The size of some clusters exceeds 1000 nm, which is ~100 times larger than the optimal degree of phase separation (~10–15 nm) defined by exciton diffusion lengths in these materials.[20,21] Therefore, the revealed nanomorphology of the PCPDE/P3HT composite is unfavourable for charge generation, and it can also cause problems for charge transport to the electrodes.

In conclusion, we have shown that phosphorus-containing fullerene derivatives such as PCPDE can be considered as promising photoactive materials for organic solar cells. The major advantage of these compounds is their higher LUMO energies arising from the unusual intramolecular interaction between the unshared electron pair of the phosphonic oxygen atom and the fullerene cage. The compound PCPDE gave moderate photovoltaic characteristics due to unfavourable morphology of its composite with the donor polymer P3HT. Further efforts will be focused on the preparation of compounds similar to PCPDE and bearing a longer alkyl chain at the phosphonic acid residue to improve the compatibility of the fullerene-based material with P3HT and afford composites with better nanomorphologies and photovoltaic performances.

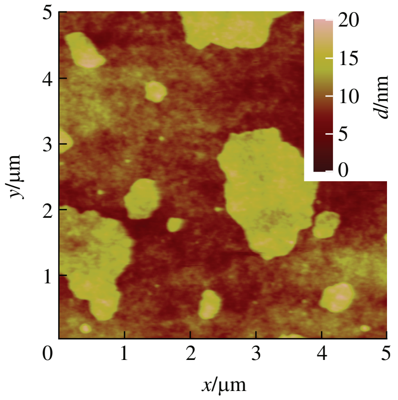

Figure 6 AFM topography image of the annealed PCPDE/P3HT composite film.

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