

Influence of the solvent on the crystal structure of PCBM[†] and the efficiency of MDMO-PPV:PCBM ‘plastic’ solar cells

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Two crystal structures of PCBM, obtained from different crystallisation solvents, are presented; a proposed link with solvent dependence of the efficiency of MDMO-PPV:PCBM solar cells is described.

Fullerenes have interesting properties that may be utilised for applications such as in photodetectors and organic photovoltaic (PV) devices.¹ In particular the bulk-heterojunction type PV-devices have received much attention recently. In this type of device, an intimate mixture of an electron donor phase (*e.g.*, a π -conjugated polymer) and an electron acceptor phase (*e.g.*, a fullerene derivative) serves as the photoactive layer.² One of the main concerns is the nano-morphology of this photoactive layer. Several approaches to obtain a favoured three-dimensional interpenetrating network are pursued, amongst them the use of soluble ‘double cable’ materials,³ fullerene containing polymers,⁴ and covalent or hydrogen bonded⁵ molecular dyads,⁶ and tryads.

Simply changing the solvent used for spincoating from toluene to chlorobenzene in the case of MDMO-PPV (poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) and PCBM⁷ (**1**, Fig. 1a) resulted in a three-fold increased AM1.5 spectrum power conversion efficiency up to 2.5%.⁸ A more intimate mixing of the components, resulting in both a larger internal donor-acceptor interface area, and/or an increased charge mobility in at least one of the components are possible explanations for this result.

Formation of methanofullerene nano-crystallites might occur upon spincoating of the photoactive blend, since phase-segregated regions are experimentally observed.⁸ Phase separation is also observed by AFM in spincoated MEH-PPV:C₆₀ blends (up to 20 wt% of C₆₀).⁹ The better PV devices were obtained from aromatic solvents, such as xylene, chlorobenzene (CB) and *ortho*-dichlorobenzene (ODCB). Recently, the formation of C₆₀ and C₇₀ clusters by injecting a fullerene solution in a ‘bad’ solvent was described.¹⁰ The narrow size distribution of the clusters formed were influenced by the concentration of fullerene used and by the choice of both solvents. Such effects may also occur during the drying process of the film upon spincoating of a PPV:PCBM blend.

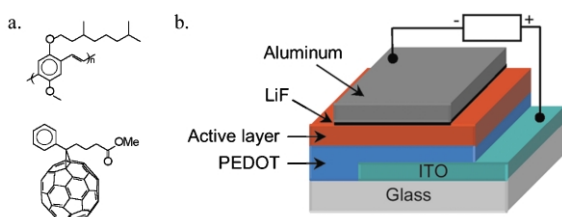


Fig. 1 a. MDMO-PPV and PCBM; b. ‘Plastic’ solar cell structure.

[†] PCBM: Phenyl-C61-Butyric acid Methyl ester. IUPAC: methyl 5-(3'*H*-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerenyl)-5-phenylpentanoate.

The lack of information about the three-dimensional morphology of the MDMO-PPV:PCBM blend prompted us to investigate the crystal structure of **1**, crystallised from ODCB and CB, and to determine a possible relation with the surface morphology of active layers of MDMO-PPV:PCBM, and with the efficiency of PV devices made thereof.

Crystallisation from ODCB gave a red-brown platelet-shaped crystal (0.25 × 0.20 × 0.02 mm).[‡] The unit cell contains eight discrete molecules (4 × **1**, 4 × ODCB, asymmetric unit 1 × **1**, 1 × ODCB, Fig. 2a). In the crystal from ODCB, layers of fullerene moieties, with a centre-to-centre distance of approximately 10 Å, separated by layers consisting of the addend and ODCB are observed (Fig. 3). Crystallisation from CB gave a reddish triangle platelet-shaped crystal (0.18 × 0.15 × 0.10 mm). In this case the unit cell consists of six discrete units (4 × **1**, 2 × CB, asymmetric unit 2 × **1**, 2 × 0.5 × CB, Fig. 2b). The CB-units have a crystallographic centre of inversion, implying disordered solvent molecules.

The crystal packing, obtained by crystallisation from CB, (Fig. 4a) did not show layers as in the case of ODCB. On the contrary, in this case all methanofullerene molecules have a fullerene–fullerene centre-to-centre distance of less than 10.13 Å, clearly demonstrating a three-dimensional network of closely packed fullerene moieties. Moreover, the shortest centre-to-centre distance between the fullerene moieties in this structure is 9.85 Å, *i.e.* less than in crystals of C₆₀ (fcc, 10.0 Å)!¹¹

If nano-crystallites of this structure are formed upon spincoating of the photoactive blend from CB, electron

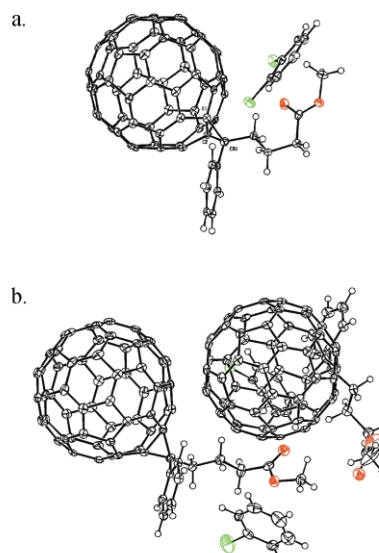


Fig. 2 Molecular structure of PCBM, crystallised from a. ODCB; b. CB. (red = oxygen, green = chlorine)

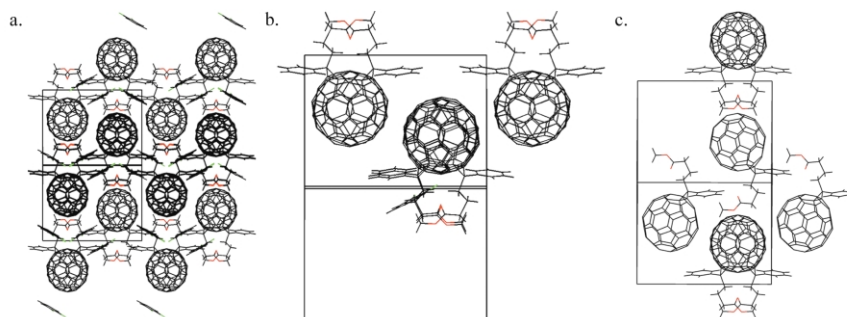


Fig. 3 Crystal packing (ODCB). a. View along the $[-1,0,-1]$ -direction, $2 \times 2 \times 2$ unit cells; b. PCBM with neighbouring moieties ($10.00 < d < 10.22$ Å ($d = C_{60}$ centre to centre distance)); c. PCBM with neighbouring moieties ($d = 12.95, 13.15$ and 13.76 Å).

transport by three-dimensional hopping can be envisioned, while hopping in the third dimension is hampered in the case of ODCB due to the increased distance between the layers.

The increased hopping probability in three dimensions, *i.e.*, mobility in the fullerene phase, can be beneficial to the efficiency of the solar cell. We have not determined the electron mobility in the tiny crystals, let alone the anisotropy factors.

The hole mobility in a film of pristine MDMO-PPV increased by an order of magnitude when spincoated from CB instead of toluene.¹² The dark current in MDMO-PPV:PCBM solar cells is proposed to be mainly an electron current on the fullerene phase, motivated by the difference in electron and hole mobility

in the pristine materials.¹³ If the phase separation in the blend would be into domains of pure constituents (*i.e.* pure donor and acceptor domains), one could speculate about the influence of the solvent on the charge carrier mobility in the phases (through different molecular packing). However, there is no proof that phase separation occurs in this way. More likely, phase separation takes place into domains with different ratios of donor and acceptor. This complicated phase separation questions the comparison of single component mobilities with those obtained from composite bulk composites.

The surface morphology of the pristine MDMO-PPV films (PFM-AFM: pulsed force mode-AFM) cast from CB or xylenes showed comparable roughness, although the one cast from CB appeared somewhat more homogeneous (Fig. 5). In contrast, blends (0.4 w/w % MDMO-PPV : PCBM = 1 : 4), spun from ODCB, CB, or xylenes, demonstrated strong dependence of the surface roughness on the spincoat solvent (Fig. 6). ODCB gave more homogeneous films (better 'fullerene-solvent') compared to CB, whereas xylenes gave rise to large defects in the form of deep pinholes (> 5 nm, 'bad' solvent).

MDMO-PPV:PCBM photovoltaic devices, as depicted in Fig. 1b, with the active layer spun from ODCB, CB, or xylenes, were constructed and measured (Table 1). The V_{oc} (open circuit voltage) obtained is identical within experimental error, as expected.¹⁴ However, a dramatic increase in I_{sc} (short circuit current) and FF (fill factor) were observed for CB, which resulted in an overall efficiency of 3.0% (uncorrected for temperature and spectral mismatch), an increase of 30% compared to xylenes.¹⁵ Both I_{sc} and FF are heavily influenced by the morphology of the photoactive blend, *i.e.*, the formation of a proper interpenetrating network. It is expected that the scale of phase separation is critical to the performance of the device. Spincoating from xylenes resulted in larger donor and acceptor domains compared to CB. Too large domains can hamper the formation of charge carriers (the exciton diffusion lengths in MDMO-PPV and PCBM are in the range of 10 nm). In the ODCB case, smaller domains are observed compared to CB, thus generating a larger interface between donor and acceptor.

In the case of highly intimate mixing, charge recombination is expected to increase, reducing the overall conversion

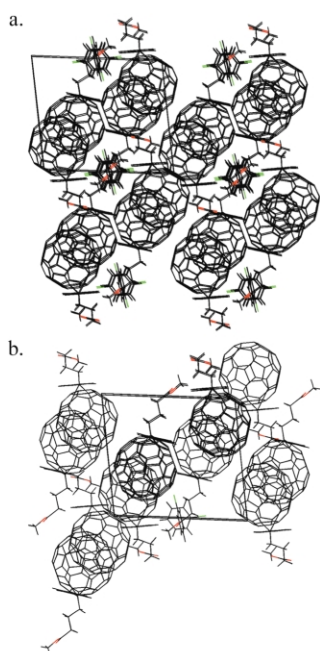


Fig. 4 Crystal packing (CB). a. View along the $[0,0,1]$ -direction, $2 \times 2 \times 2$ unit cells; b. PCBM with neighbouring moieties ($9.85 < d < 10.13$ Å).

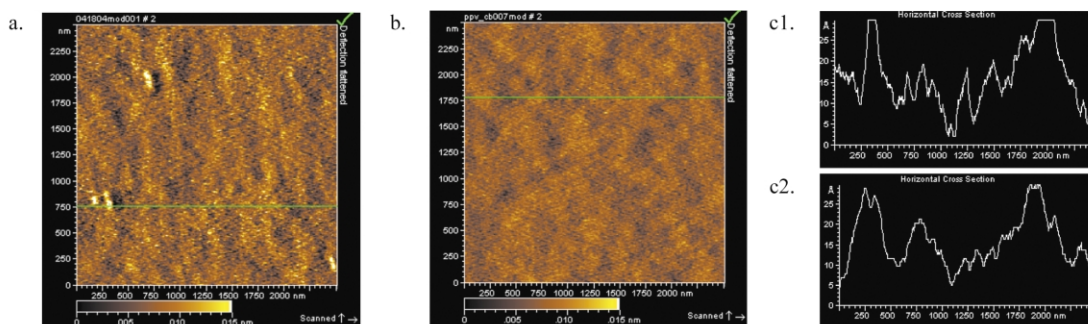


Fig. 5 PFM-AFM topography pictures spincoated from 0.25% solutions. a. toluene, b. CB. c. surface profile from toluene (c1) and CB (c2).

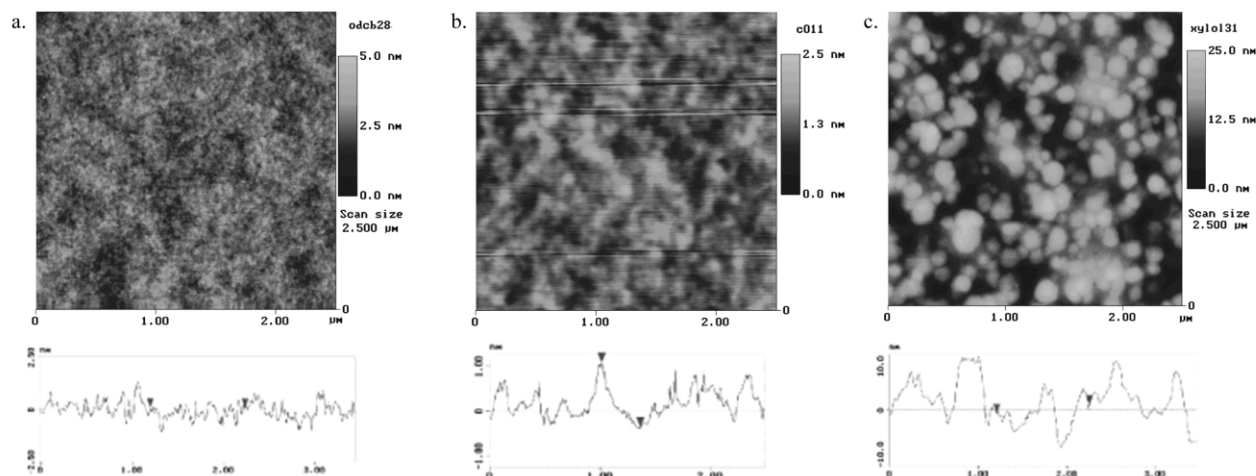


Fig. 6 Surface of MDMO-PPV : PCBM (1 : 4 wt. ratio) composites, spincoated from 0.4 polymer wt.% solutions. a. ODCB; b. CB; c. xylenes. Note the different scales in the respective profiles.

Table 1 Photovoltaic parameters of MDMO-PPV : PCBM (1 : 4) devices^a

0.40 w/w % MDMO- PPV	V_{oc}/mV	I_{sc}/mA cm^{-2}	FF	η (%)	I at -2 V/mA cm^{-2}	I at $+2$ V/mA cm^{-2}	Area/ mm^2
ODCB	796	4.46	0.5171	2.294	6.76	301	5.25
CB	802	5.37	0.5628	3.034	6.90	268	5.55
Xylenes	816	4.16	0.4922	2.09	5.82	172	4.76

^a Illumination: 80 mW cm^{-2} white light (AM1.5 solar simulator, 55 °C). Obtained values are the mean of at least nine cells. Efficiencies are uncorrected.

efficiency. PV results, obtained with molecular dyads as (single) active layer constituents, clearly point in this direction.⁶

In conclusion, for various reasons CB seems to be the optimal solvent in preparing MDMO-PPV:PCBM PV cells. First, single crystals of PCBM (electron acceptor) grown from CB show crystal packing in which the electrons can hop easily in three dimensions. Second, CB has a beneficial effect on the hole mobility in the electron-donor, compared to toluene. Third, CB seems to be the solvent of choice to obtain a blend morphology with optimal functionality. The latter effect of CB on the performance of the cell is likely the most important one. Further analysis of the microstructure of the blend is currently underway. A power efficiency of 3.0% (uncorrected) has been obtained in the case of CB.

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Notes and references

† Single crystals of PCBM were obtained from either dichlorobenzene (ODCB) or chlorobenzene (CB), $T = 90$ K. Crystal data: a. Crystallised from ODCB: $C_{72}H_{14}O_2 \cdot C_6H_4Cl_2$, $M = 1057.91$, monoclinic, $a = 13.7565(9)$, $b = 16.634(1)$, $c = 19.077(1)$ Å, $\beta = 105.289(1)^\circ$, $U = 4210.8(4)$ Å³, $P2_1/n$, $Z = 4$, $D_x = 1.669$ g cm^{-3} , $\mu(Mo-K\alpha) = 2.21$ cm^{-1} , $F(000) = 2144$, $wR(F^2) = 0.0701$ for 9661 reflections and 811 parameters and $R(F) = 0.0442$ for 4425 reflections obeying $F_o \geq 4.0\sigma(F_o)$ criterion of observability. CCDC 211976; b. Crystallised from CB: $2(C_{72}H_{14}O_2 \cdot 0.5(C_6H_5Cl))$, $M = 1934.21$, triclinic, $a = 13.8333(9)$, $b = 15.288(1)$, $c = 19.249(1)$ Å, $\alpha = 80.259(1)$, $\beta = 78.557(1)$, $\gamma = 80.406(1)^\circ$, $U = 3894.9(4)$ Å³, $P\bar{1}$, $Z = 2$, $D_x = 1.648$ g cm^{-3} , $\mu(Mo-K\alpha) = 1.31$ cm^{-1} , $F(000) = 1964$, $wR(F^2) = 0.1184$ for 15737 reflections and 1544 parameters, and $R(F) = 0.0532$ for 9339 reflections obeying $F_o \geq$

$4.0\sigma(F_o)$ criterion of observability. Figures were made using PLATON,¹⁶ CCDC 211977. See <http://www.rsc.org/suppdata/cc/b3/b305988j/> for crystallographic data in CIF or other electronic format.

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