

## High mobility n-channel organic field-effect transistors based on soluble C<sub>60</sub> and C<sub>70</sub> fullerene derivatives

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### ABSTRACT

We report on n-channel organic field-effect transistors (OFETs) based on the solution processable methanofullerenes [6,6]-phenyl-C<sub>61</sub>-butyric acid ester ([60]PCBM) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester ([70]PCBM). Despite the fact that both derivatives form glassy films when processed from solution, their electron mobilities are high and on the order of 0.21 cm<sup>2</sup>/V s and 0.1 cm<sup>2</sup>/V s, for [60]PCBM and [70]PCBM, respectively. Although the derived mobility of [60]PCBM is comparable to the best values reported in the literature, the electron mobility of [70]PCBM is the highest value reported to date for any C<sub>70</sub> based molecule. We note that this is the only report in which C<sub>60</sub> and C<sub>70</sub> methanofullerenes exhibit comparable electron mobilities. The present findings could have significant implications in the area of large-area organic electronics and organic photovoltaics where C<sub>60</sub> derivatives have so far been the most widely used electron acceptor materials.

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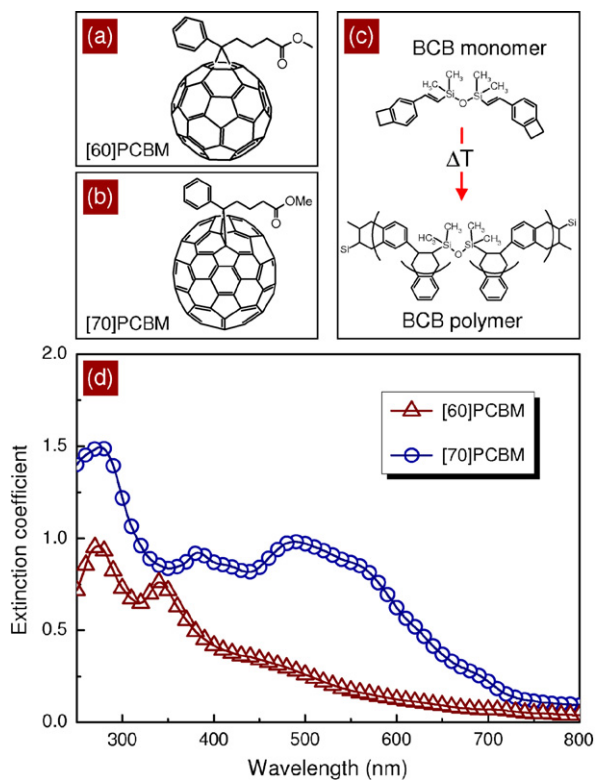
For the development of the next generation organic integrated circuits (ICs) logic gates with improved noise margin (NM) and lower power dissipation are required [1,2]. Both parameters are of critical importance since wide NM enables large-scale integration of organic field-effect transistors (OFETs) with acceptable manufacturing yield while low power dissipation qualifies organic ICs for battery-powered (i.e. portable) applications. One technology that could potentially meet these needs is the complementary logic [1]. In the latter, electron transporting (n-channel) and hole transporting (p-channel) OFETs are combined to produce high-performance circuits with high manufacturing yield and excellent power dissipation characteristics [2,3]. A significant technological challenge, however, associated with organic complementary circuits is the deposition and patterning of the p- and n-channel semiconductors with high resolution. The latter represents the main technological bottleneck and would need to be addressed before complementary logic can be adopted for the next generation organic ICs.

The vast majority of organic complementary circuits reported in the literature to-date are based on thermally evaporated p-

channel/n-channel semiconductors [1–4]. Although, an excellent proof of concept practical implementation of the technology in large-scale ICs is limited due to design constraints imposed by the shadow masking utilised for semiconductor patterning. In this context, alternative deposition techniques (i.e. ink-jet printing, gravure printing, etc.) could potentially provide a long-term solution. In an effort to address this issue, significant research has focused on the synthesis of organic semiconductors with useful solubility [5]. As a result, a number of soluble p-channel semiconductors with carrier mobilities comparable to amorphous silicon (a-Si) have been demonstrated and utilised in unipolar ICs [6,7]. On the other hand, progress in the area of soluble n-channel semiconductors has been much slower with relatively few successful demonstrations [8–12]. This distinct lack of soluble n-channel semiconductors has, to a large extent, hindered the development of large-scale organic complementary ICs.

Here, we report on high mobility n-channel OFETs based on two rather known fullerene derivatives, namely [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester ([60]PCBM) [Fig. 1(a)] and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester ([70]PCBM) [Fig. 1(b)]. Both molecules are soluble in a variety of organic solvents and hence suitable for solution processing. The transport characteristics of the two molecules are evaluated in top-contact,

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**Fig. 1.** Chemical structure of [60]PCBM (a), and [70]PCBM (b) methanofullerenes. (c) Chemical structure of the BCB before (monomer) and after (polymer network) curing. (d) UV-vis absorption spectra obtained from thin films of [60]PCBM and [70]PCBM.

bottom-gate transistor architectures, employing a suitable polymer gate dielectric and low workfunction source/drain (S/D) electrodes. Despite the differences in the electronic structure of the two methanofullerenes their electron mobilities are similar with maximum values in the range 0.1–0.21 cm<sup>2</sup>/V s. These are among the highest electron mobilities reported to date for OFETs based on solution processable organic semiconductors.

Top-contact, bottom-gate transistors were fabricated on glass substrates coated with an indium tin oxide (ITO) layer (120 nm) acting as the gate electrode. Divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB), purchased from Dow Chemicals, was spin cast (2000 rpm, room temperature) on the top of the quartz/ITO substrate as the gate dielectric. The BCB monomer layer was then cured (crosslinked) at 280 °C under N<sub>2</sub> for sixteen hours to form a polymeric network [13]. The chemical modification of the BCB monomer to a polymeric network upon heating is shown in Fig. 1(c). Following, films of [60]PCBM and [70]PCBM (Solenne B.V.) were spin cast directly from chlorobenzene solutions (10 mg/ml wt%) at room temperature in N<sub>2</sub> atmosphere. Finally, bilayer top contact electrodes consisting of Ca/Al (20 nm/40 nm, respectively) were evaporated under high vacuum (10<sup>-6</sup> mbar) through a shadow mask. The channel length (*L*) and width (*W*) of the transistors was 60 μm and 1–1.5 mm, respectively. Electrical measurements were performed at room temperature under N<sub>2</sub> using an HP4156C semiconductor parameter analyser.

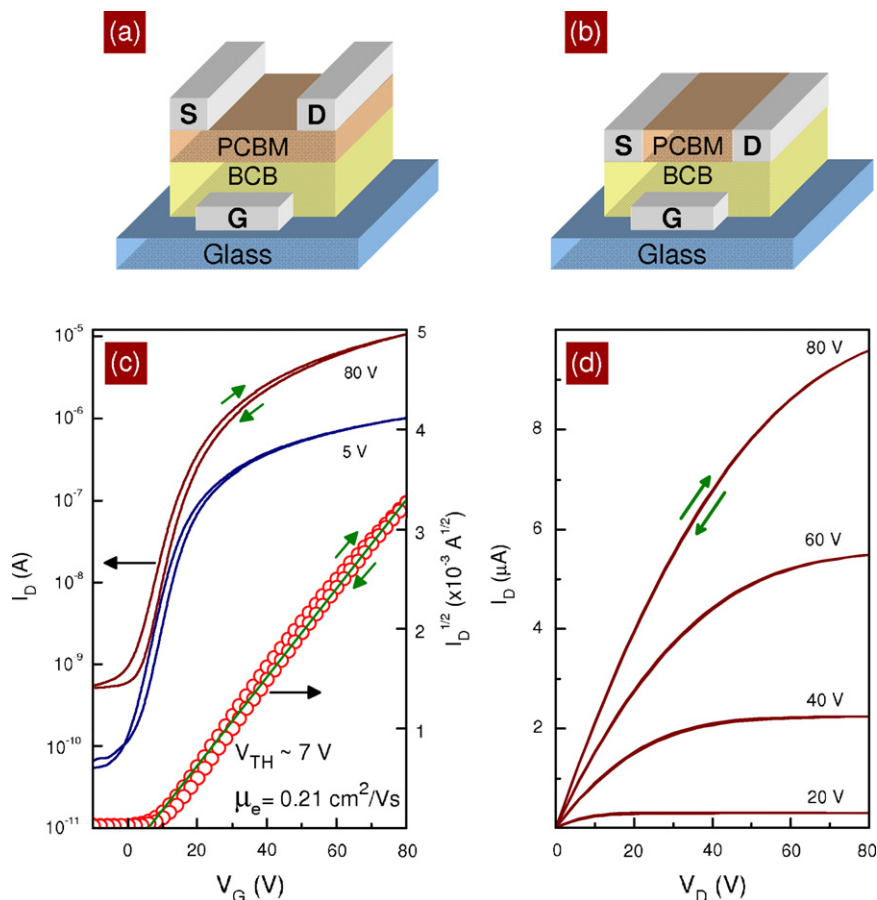
Fig. 1(d) shows the UV-vis absorption spectrum of [60]PCBM and [70]PCBM films spin coated on quartz substrates. As can be seen, the onset of absorption is similar for both molecules with the [70]PCBM exhibiting a significantly stronger absorption coefficient. This observation is in agreement with earlier measurements

obtained from solutions [14]. By combining the optical data of Fig. 1(d) with electrochemical measurements reported earlier [10] and assuming an exciton binding energy of 0.3–0.4 eV, approximate values for the lower unoccupied molecular orbital (LUMO) and higher occupied molecular orbital (HOMO) levels were calculated yielding LUMOs in the range 3.5–3.8 eV and HOMOs in the range 5.7–6.1 eV. The high electron affinities of the two compounds make them suitable for use in n-channel OFETs since electron injection from low workfunction S/D electrodes into the LUMO should be possible. Indeed, earlier work by the authors [15,16], and other workers [17,18], has demonstrated transistor and circuit operation with good performance characteristics. We note, however, that the large majority of these studies focussed on [60]PCBM transistors due to the availability of [60]PCBM whereas reports on [70]PCBM OFETs are very scarce [19].

To further study and compare the electron transport characteristics of the two methanofullerenes we fabricated OFETs employing the device structure shown in Fig. 2(a). We first discuss the operating characteristics of [60]PCBM OFETs with *L* = 60 μm and *W* = 1 mm. Fig. 2(c) shows the evolution of drain current (*I<sub>D</sub>*) versus gate bias (*V<sub>G</sub>*), measured at different drain voltages (*V<sub>D</sub>*). The transfer characteristic measured at *V<sub>D</sub>* = 5 V corresponds to the linear operating regime, while the curve measured at *V<sub>D</sub>* = 80 V relates to the saturation regime. As can be seen, transistor operation exhibits negligible hysteresis with maximum calculated electron mobility on the order of 0.21 cm<sup>2</sup>/V s. Moreover, the current on–off ratio is relatively high (>10<sup>4</sup>) and the threshold voltage (*V<sub>TH</sub>*), calculated from the *I<sub>D</sub>*<sup>1/2</sup> versus *V<sub>G</sub>* plot, approximately 7 V. We note that the electron mobility derived here is among the highest values reported to date for soluble fullerene derivative [11,12,18], and roughly 20–30 times lower than the best values reported for evaporated films of C<sub>60</sub> [20,21].

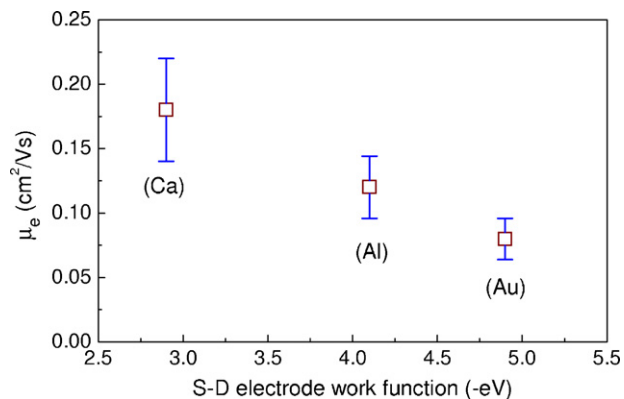
Fig. 2(d) shows the output operating characteristics obtained from the same transistor at room temperature in N<sub>2</sub>. Negligible hysteresis is observed with the Ca/Al electrodes exhibiting good ohmic behaviour, as is evident from the linearity of the characteristics at low *V<sub>D</sub>*. The performance of [60]PCBM OFETs was found to depend both on the device architecture as well as on the type of S–D electrodes. For example, when instead of the top-contact, bottom-gate device structure, a bottom-contact, bottom-gate architecture [Fig. 2(b)] is employed (i.e. the S/D electrodes are deposited on top of the BCB layer followed by the deposition of the semiconductor), the electron mobility and the current on–off ratio decrease to values 10<sup>-3</sup>–10<sup>-2</sup> cm<sup>2</sup>/V s and 10<sup>3</sup>, respectively (data not shown). Similarly, when electrodes with higher workfunction – such as aluminium and gold – are employed, the electron mobility reduces to 0.08 cm<sup>2</sup>/V s, while the current on–off ratio increases to ~10<sup>5</sup>. The influence of the electrode workfunction on electron mobility is shown in Fig. 3. Similar effects have been reported in the literature for different material systems and were also ascribed to contact effects [12,22].

Earlier studies on C<sub>70</sub> OFETs [23,24], as well as [70]PCBM OFETs [19], have consistently reported electron mobilities lower than values obtained from transistors based on C<sub>60</sub> [20] and its derivatives [15,18]. These results were attributed to the difference in the electronic structure of the two fullerenes [23]. To test whether this interpretation is valid for optimised transistor architectures, we have fabricated [70]PCBM OFETs using the device structure shown in Fig. 2(a) with *L* = 60 μm and *W* = 1.5 mm. A typical set of the transfer and output characteristics is shown in Fig. 4. Good electron transport characteristics are evident with ohmic-like contact behaviour and electron mobility, measured in saturation, of ~0.1 cm<sup>2</sup>/V s. This is a surprisingly high value and compares favourably with the electron mobility of [60]PCBM. In an effort to study this further, we carried out extensive control experiments



**Fig. 2.** The bottom-gate, top-contact (a) and the bottom-gate, bottom-contact (b) transistor architectures studied. (c) Transfer characteristics of a [60]PCBM transistor ( $L = 60 \mu\text{m}$ ,  $W = 1 \text{mm}$ ) employing a bottom-gate, top-contact architecture. (d) Output characteristics obtained from the same [60]PCBM transistor.

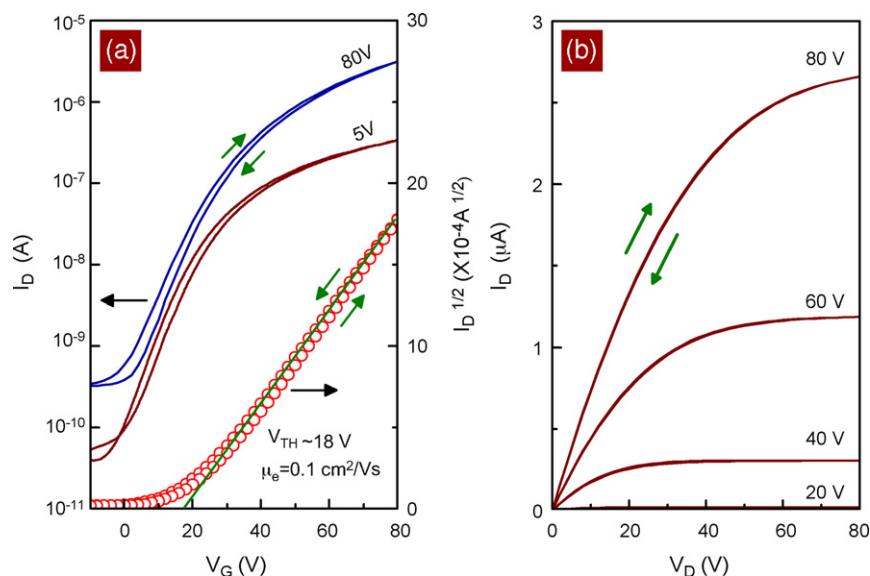
in which [60]PCBM and [70]PCBM transistors were fabricated in a parallel process. In all experiments we were unable to observe any significant and reproducible differences in the electron mobilities obtained from the two derivatives. One possible explanation for this observation is that although the intrinsic mobility of the  $C_{60}$  derivative is higher the solubility of [70]PCBM (40 mg/ml, chlorobenzene) is much higher than [60]PCBM (25 mg/ml, chlorobenzene). The consequence of this could be that [70]PCBM forms a better interface with the dielectric layer leading to enhanced mobilities. Ongoing work is focussing on elucidating the effects of material solubility and film morphology.



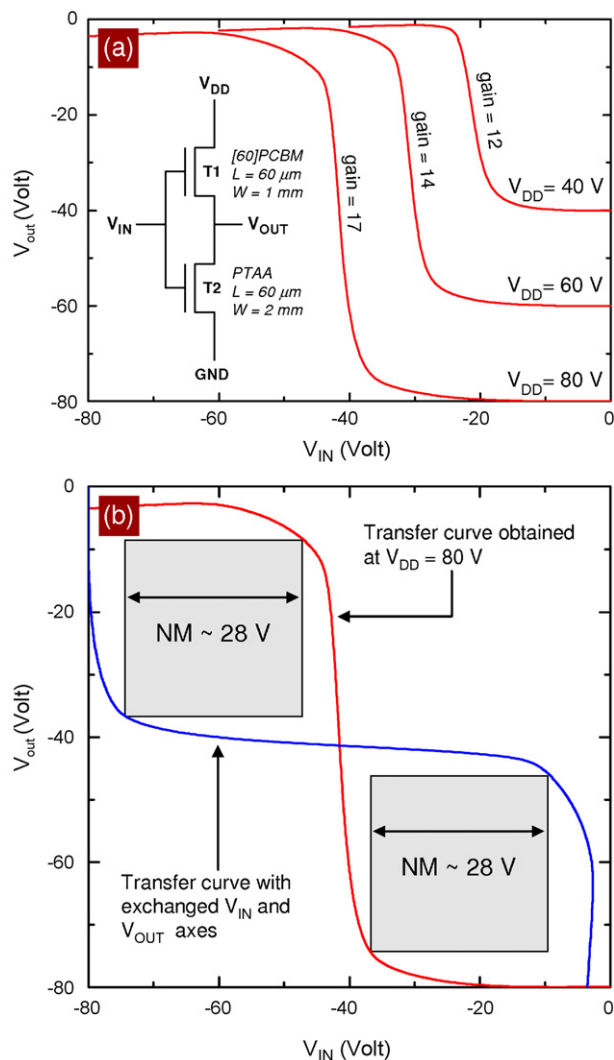
**Fig. 3.** Electron mobility spread versus workfunction of the source–drain (S–D) electrode materials.

It is evident from the present results that it can no longer be assumed that the electron mobility of [70]PCBM is significantly lower than that of [60]PCBM. This finding could have significant implications not only for the use of [70]PCBM in organic ICs but also for its application in OPVs where high absorption coefficients are required [see Fig. 1(d)]. This argument is inline with the recent demonstration of high performance OPVs based on polymer:[70]PCBM blends [25,26].

Using the [60]PCBM and [70]PCBM transistors discussed earlier in combination with p-channel OFETs, based on polytriarylamines (PTAA), we have also been able to fabricate complementary voltage inverters with excellent operating characteristics. The n-channel and p-channel OFETs were fabricated in two separate silicon substrates chips and interconnected using metal wires. Fig. 5(a) shows the transfer curves of a voltage inverter based on a [60]PCBM (T1) and a PTAA (T2) OFET. Despite the different carrier mobilities and the small difference in the  $W/L$  ratios between the two transistors, tuning of the threshold voltage in the PTAA OFET allows the design of inverters with symmetric trip point. However, such an approach would be inappropriate for the design of truly complementary circuits since the dynamic response of the inverter will be severely effected by the transistor with the lowest mobility, i.e. the PTAA OFET ( $\sim 1 \times 10^{-2} \text{cm}^2/\text{Vs}$ ). The maximum voltage gain (defined as  $dV_{\text{OUT}}/dV_{\text{IN}}$ ) measured from Fig. 5(a) is  $\sim 17$  and depends on the supply voltage ( $V_{\text{DD}}$ ). The NM of the inverter was also calculated (at  $V_{\text{DD}} = 80 \text{V}$ ) as the side of the largest square that can be ascribed between the transfer characteristics and the same curve re-plotted with exchanged input and output axes [27]. This plot, from which the noise margin of 28 V can be estimated, is shown in Fig. 5(b).



**Fig. 4.** (a) Transfer characteristics of a [70]PCBM transistor ( $L=60\ \mu\text{m}$ ,  $W=1.5\ \text{mm}$ ) employing a bottom-gate, top-contact architecture. (b) Output characteristics obtained from the same [70]PCBM transistor.



**Fig. 5.** (a) Quasistatic transfer characteristics of a complementary voltage inverter based on an n-channel [60]PCBM transistor T1 ( $L=60\ \mu\text{m}$ ,  $W=1\ \text{mm}$ ) and a p-channel PTAA ( $\sim 0.01\ \text{cm}^2/\text{Vs}$ ) transistor T2 ( $L=60\ \mu\text{m}$ ,  $W=1.5\ \text{mm}$ ). (b) Noise margin calculated for the same inverter at  $V_{\text{DD}} = -80\ \text{V}$ .

The latter is approximately 70% of its maximum theoretical value (at  $V_{\text{DD}} = 80\ \text{V}$ ) given as  $\text{NM}_{\text{MAX}} = V_{\text{DD}}/2 = 40\ \text{V}$  and can be considered very high when compared with standard unipolar (p-type) organic inverters [27].

In summary, we demonstrated n-channel OFETs based on the fullerene derivatives [60]PCBM and [70]PCBM with maximum electron mobilities of 0.1–0.21  $\text{cm}^2/\text{Vs}$ . This is the first study in which the two methanofullerene are found to exhibit similar electron mobilities. The present findings are important not only for the use of these molecules in organic microelectronics but also for their application in organic photovoltaics where [60]PCBM has so far been the most widely used electron acceptor compound.

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