Supplementary Material for

Molecular dynamics simulations of the solvent- and thermal history-dependent structure of the PCBM fullerene derivative

Francesco Frigerio[a#], *Mosè Casalegno*[b#], *Chiara Carbonera*[c], *Tommaso Nicolini*[b], *Stefano Valdo Meille*[b] *and Guido Raos*[b]*

[a] francesco.frigerio@eni.com, ENI Refining and Marketing, via Maritano 26, I-20097 San Donato Milanese (MI), Italy

[b] mose.casalegno@chem.polimi.it, guido.raos@polimi.it, valdo.meille@polimi.it, tommaso.nicolini@chem.polimi.it, Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Politecnico di Milano, via Mancinelli 7, I-20131 Milano (MI), Italy

[c] chiara.carbonera@eni.com, Research Centre for Non-Conventional Energies, ENI Istituto Donegani, Via Fauser 4, I-28100 Novara (NO), Italy.

Density measurements

Density measurements on samples of solvent-free PCBM were carried out by flotation in aqueous NaI solutions. A sample purchased from Aldrich (>99% purity, cat. 668430) was used. Powder diffraction patterns (Figure S1) measured on a θ/θ Italstructures diffractometer of the as purchased PCBM were identical to those reported in the literature [1S, 2S] for similar products, showing a very high crystallinity. All the density values reported below are based on at least three different measurements. For the crystalline sample a value of 1.613±0.006 Mg/m^3 was determined. Three different procedures were used to prepare amorphous samples. Quenching from the melt into a dry ice-acetone bath and quenching at controlled rate of 400°C/min from 300°C to 120°C in a Perkin-Elmer DSC 8500 gave samples with a density of 1.50±0.02 Mg/m^3. Quenching at a controlled rate of 300°C/min from 300°C to 120°C gave samples with a slightly higher density, namely 1.52±0.02 Mg/m^3.

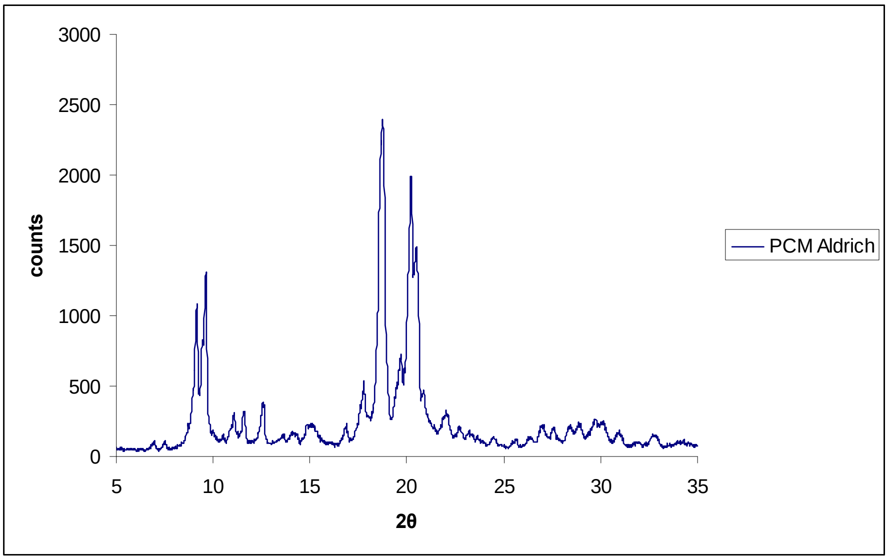
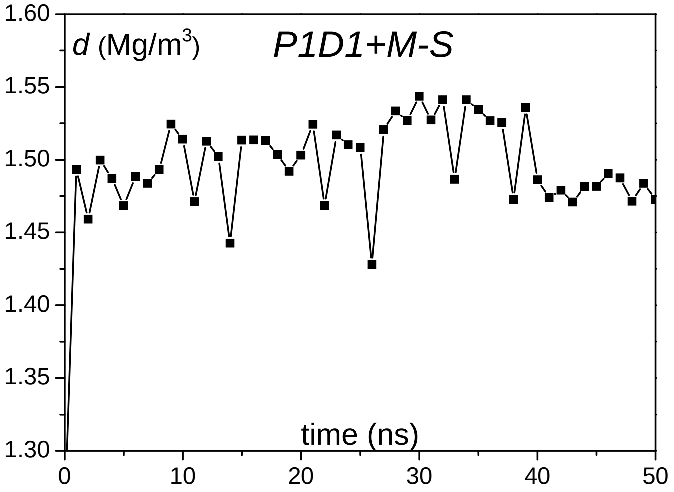


Figure S1: Powder diffraction pattern (Cu-Kα) of the PCBM sample used for density measurements, as acquired from Aldrich.

Convergence of the simulated densities

Figure S2 shows the time dependence of the density, from the NPT simulations of the P1D1+M-S and P2M1+M-S systems. The initial states are taken from the simulations of amorphous PCBM containing the respective solvent molecules. These solvent molecules were deleted and the MD simulations restated, with target temperature T=400 K and pressure P=1atm. In both cases, there is an abrupt increase in density within the first ns of simulations, as the voids left by the solvent are filled up. After that, we observe substantial thermal fluctuations, but as a whole the densities appear to be stable, especially over the last 10 ns (the plots contain the instantaneous densities, recorded every ns; analogous plots of the "batch averages" would be much smoother). The last points of each trajectory were used to start the final NVT simulations.



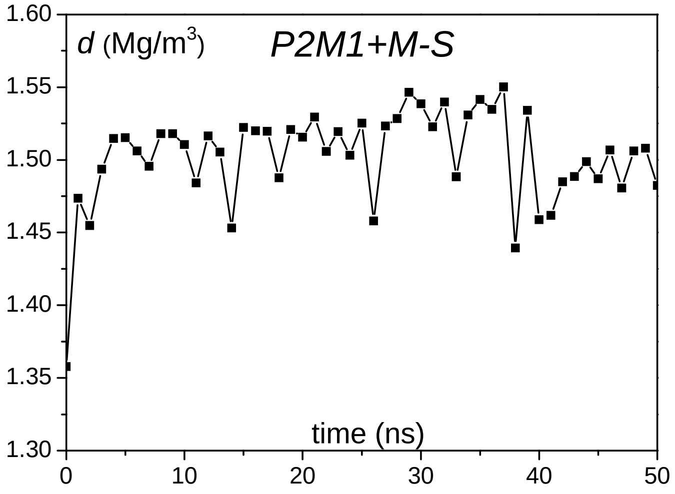


Figure S2: Time dependence of the densities, from the NPT simulations of P1D1+M-S (top) and P2M1+M-S (bottom).

Nanocrystalline and amorphous diffraction calculation

Diffraction patterns were calculated for various structures resulting from the simulation runs at 400K assuming that such structures represent nanocrystalline organization, rather than fully amorphous systems. Patterns were simulated assuming average crystallite size of 3-8 nm and appropriate peak shapes, usually applying to systems which, like polymers, crystallize with difficulty. A typical diffraction pattern example, specifically calculated for 8 nm crystals from the P1D1+M-S model (i.e. the DCB-PCBM cocrystal molten at 560 K, deprived of the solvent molecules and brought to 400K) is shown in Figure S3. Similar patterns are obtained from the other solvent-free systems described in Table 2.

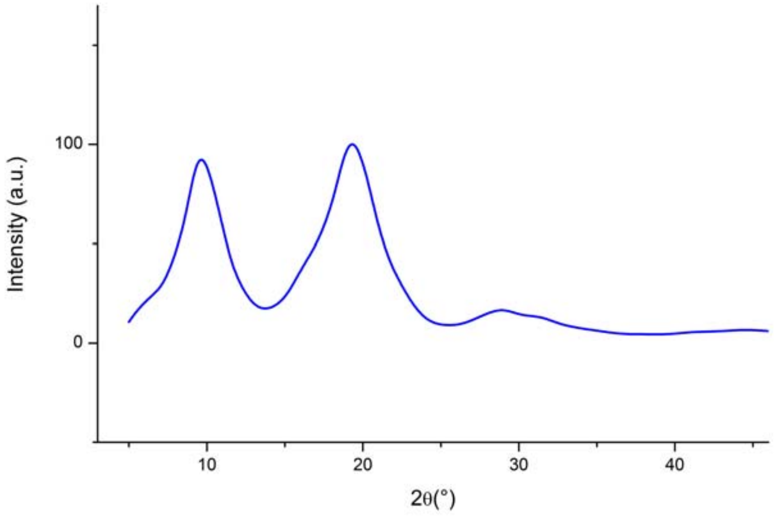


Figure S3: Typical calculated powder diffraction pattern (Cu-Kα) for nanocrystalline PCBM models (specifically P1D1+M-S). The three main maxima agree reasonably well with those typically observed in experimental patterns of amorphous [1S,2S] and nanocrystalline [3S] PCBM samples.

The intensity distribution differs somewhat from published patterns of fully amorphous PCBM [S1,S2], because of the overestimated intensity of lower angle peak. The positions of the main diffraction maxima show however reasonable correspondence. The calculated maxima are at 2θ =9.7, 19.3 and 28.9°, corresponding to d=0.91, 0.46 and 0.31 nm, to be compared to the experimental values of 2θ=10.3, 19.4 and 28.8° [S1], or 2θ=10.1, 19.7 and 28.5° [S2], or d = 0.46 and 0.31 nm [S3] (the last set of data comes from electron diffraction, the former two from X-ray diffraction). The somewhat larger discrepancy in the position of the lower angle peak, which is shifted to lower angles in the calculated pattern, is reasonably consistent with the thermal expansion of PCBM, since the simulations were carried out at 400 K while the experimental data were collected at room temperature.

References

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