Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Do charges delocalize over multiple molecules in fullerene derivatives?

Electronic Supplementary Information

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Table S1. Thermally averaged IPR (Boltzmann) obtained by applying a scaling factor γ to the transfer integrals (*J*) in our calculations. Quite irrespectively of the applied scaling, electrons are delocalized in C60x and localized in the other systems at room temperature. The qualitative difference between C_{60} and PCBMs is therefore imputable to the large difference in diagonal electrostatic disorder, attesting the robustness of our result against possible inaccuracies in the estimates of *J*.

γ	C60x	C61x	C61a	C71a
0.5	6.9	1.1	1.0	1.0
1.0	26.1	1.2	1.0	1.0
2.0	47.7	1.9	1.1	1.8

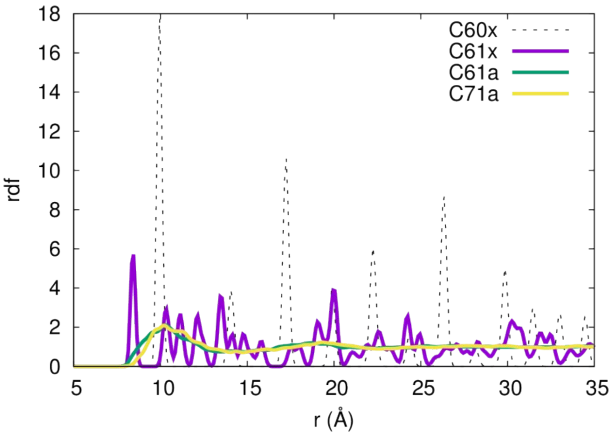

Figure S1. Radial distribution function calculated for the four samples from 20 ns MD simulation. The series of well resolved peaks of C60x and C61x testifies the long-range positional order of crystalline samples. In amorphous C61a and C71a two coordination shell are detected at ~10 and ~18 Å.

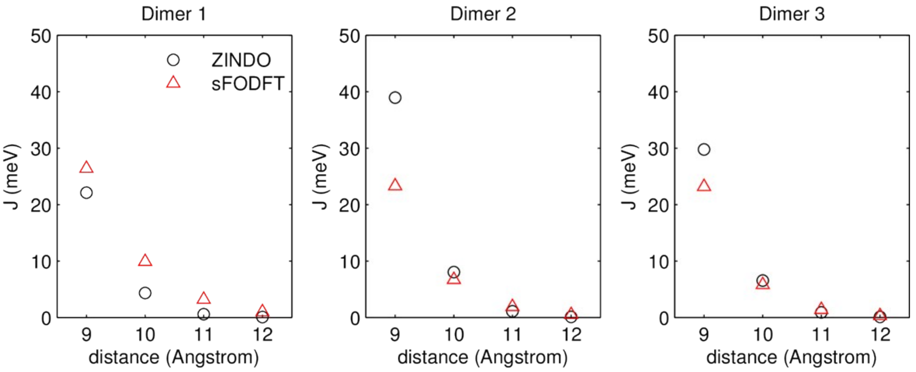

Figure S2. Comparison between scaled Fragment Orbital DFT (sFODFT) and ZINDO electron transfer integrals for C_{60} dimers. sFODFT proved an excellent correlation with high-level ab initio calculations and a quantitative match upon application a scaling factor 1.348.[1] ZINDO values are computed as one-electron couplings between LUMO orbitals (mean absolute values of the elements of the 3x3 coupling matrix between the 3 LUMOs of C_{60}). The comparison is performed for three C_{60} dimers at different mutual molecular orientation, whose geometries and sFODFT *J* values are provided in Ref. 2.

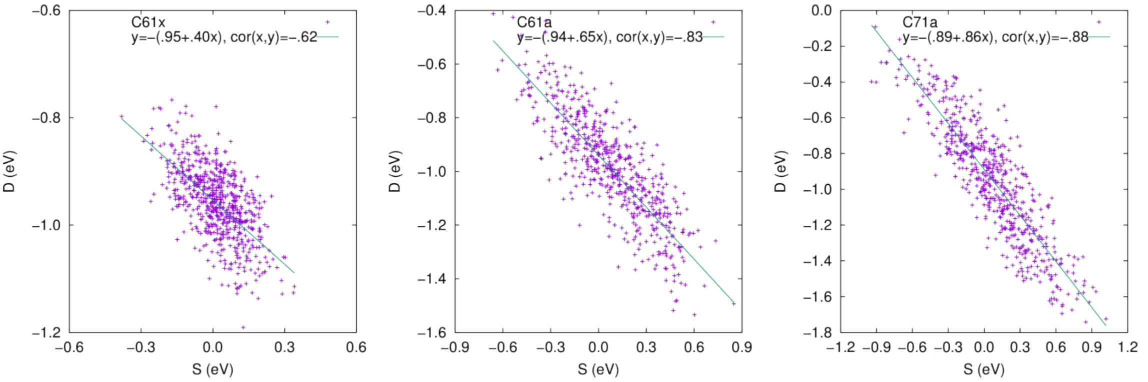

Figure S3. Correlation plots between the electrostatic (*S*) and induction (*D*) components of the polarization energy for PCBM samples. The linear regression parameters and the negative correlation coefficient are annotated in each plot.

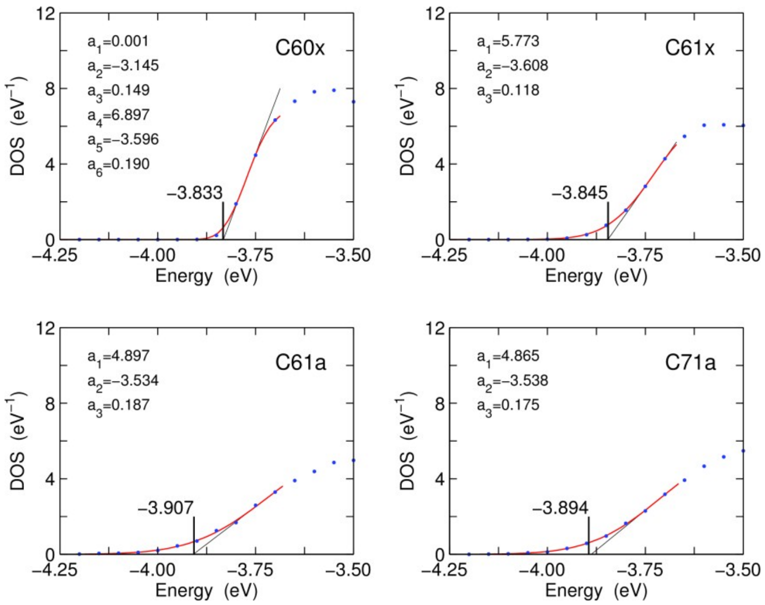

Figure S4. Fit of the low-energy tail of the DOS of delocalized states. The blue dot are the numerical DOS (histograms) obtained from the collection of the eigenvalues of Hamiltonian (1) corresponding to different time frames. The red lines show the fitting function, the black line is the tangent in its steepest point. The intercept of the tangent line on the x-axis marks the electron affinity (annotated).

The tail of the normalized DOS is fitted by the following expression:

$$y(x) = a_1 \exp\left[-\frac{(x-a_2)^2}{2a_3^2}\right] + a_4 \exp\left[-\left(\frac{x-a_5}{a_6}\right)^4\right]$$

. Least square fit parameters are annotated in each graphs, for C61x, C61a and C71a we imposed $a_4 = a_5 = a_6 = 0$.

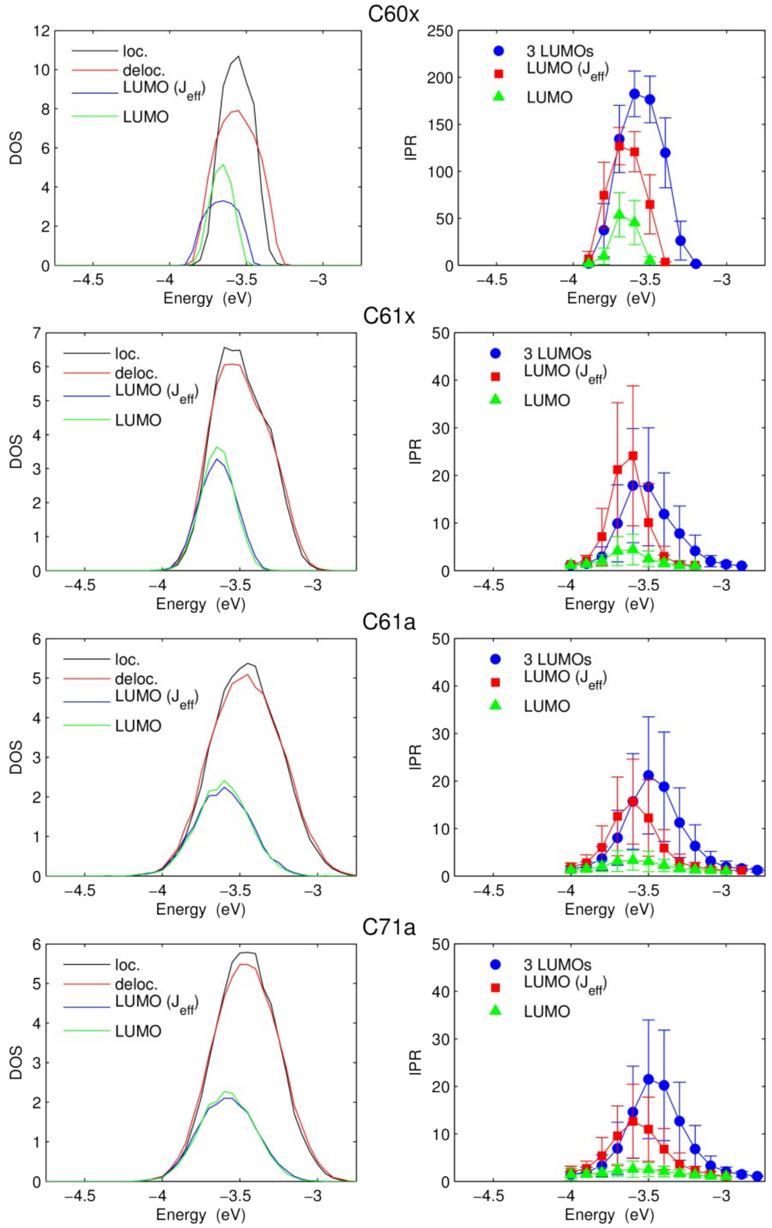

Figure S5. DOS (left panels) and corresponding IPR distribution (right panels) for the four systems, computed for localized states, delocalized states (three-orbital model), LUMO-only model and LUMO-only model with effective coupling ($J_{eff}^{mn} = \sqrt{\sum_{kl}(J_{mn}^{kl})^2/3}$, with *m* and *n* running on molecular sites and *k* and *l* on the unoccupied orbitals). LUMO-only models underestimate the maximum IPR values at the center of the DOS, though the use of effective coupling provides a satisfactory description of the DOS tail and IPR values in this low-energy window. Electron delocalization has very little effect in PCBM systems and does not appreciably alter the DOS with respect to the localized one.

References

1 A. Kubas, F. Hoffmann, A. Heck, H. Oberhofer, M. Elstner and J. Blumberger, *J. Chem. Phys.*, **140**, 105, 2014,.

2 F. Gajdos, S. Valner, F. Ho, J. Spencer, M. Breuer, A. Kubas, M. Dupuis and J. Blumberger, *J. Chem. Theroy Comput.* **10**, 4653, 2014.