Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Material

Predicting the properties of a new class of host-guest complexes: C_{60} fullerene and CB[9] cucurbituril

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1.0 – Further Computational Details

All in-water simulations were performed in the *NPT* ensemble with *T* = 298 *K* and *P* = 1 atm. The systems consisted of nearly 1200 (or 1400) water molecules and one C_{60} molecule (or C_{60}@CB[9] complex) in a cubic box with periodic boundary condition employing the minimum image convention.[1] The TIP3P potential[2] was used for the water molecule. C_{60} molecule was modeled using a based CHARMM36 force field adapted from Rivelino et.al.[3] Properties were calculated from simulations considering a time-step of 2 fs with data collected every 0.05 ps. The cubic cells were equilibrated for 1 ns and for the equilibration process we have performed a running length of 10 ns for each thermodynamical window, both in the NPT ensemble. The system was kept at the appropriate temperature and pressure via velocity rescaling[4] and Parrinello-Rahman[5] schemes, with a constant coupling of 0.1 and 1.0 respectively. All bond lengths were constrained via the LINCS algorithm.[6] A cutoff distance of 1.2 nm for LJ interaction was employed, whereas the Coulomb interactions were treated by using the PME algorithm.[7]

2.0 – PM6 molecular dynamics

The graphs of the potential energy and variation of total energy (Figure S1) confirm the stability of the semi-empirical PM6 molecular dynamics.

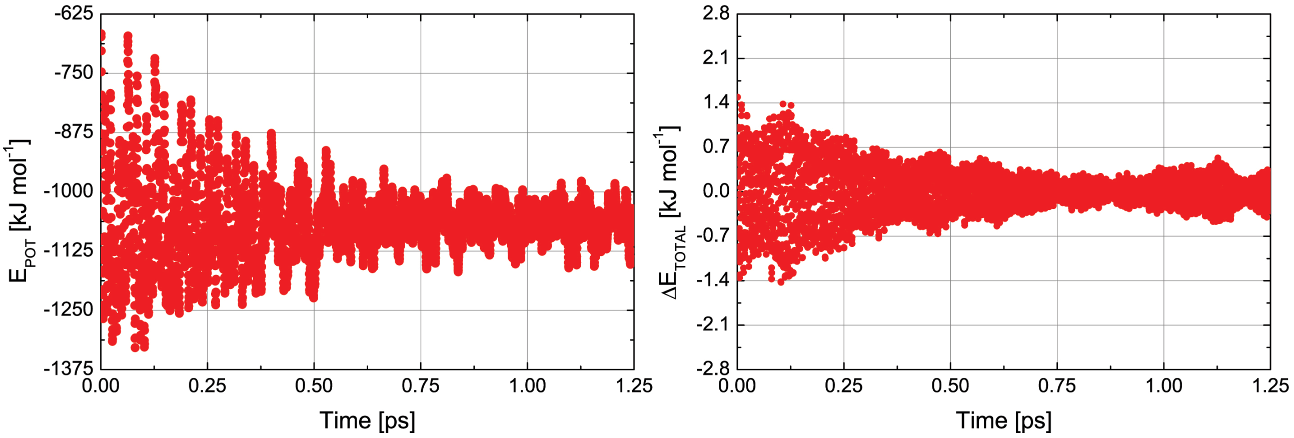

Figure S1: Potential energy and variation of the total energy (in kJ mol^{-1}) as a function of time.

2.1 – Further structural properties

During the process of inclusion some selected geometric parameters were analyzed. We observe that the largest variation for any bond distances was only 0.0013 nm while the largest variation for any angle was 4.1°. This small variation between distances and angles leads to a greater change in the structure of the CB[9] as a whole. For example, consider the top diameter, D_A, (entrance door of the fullerene) and the bottom diameter, D_B, (Figure S2 for the CB[9]). We observed through the scan calculation that as the C_{60}

enters into the CB[9] cavity the D_A diameter extends by 0.20 nm as the D_B diameter shortens by 0.05 nm (see Table S1).

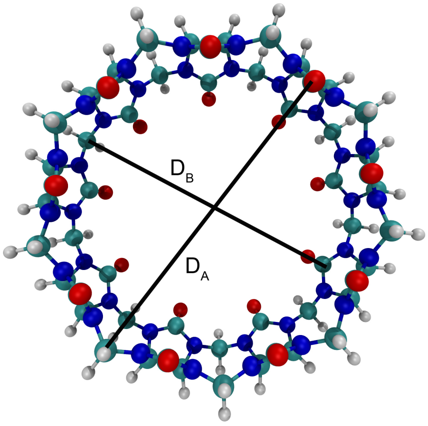

Figure S2: Representation of CB[9] and C_{60} diameter D_A (superior) and D_B (inferior)

	ΔR_{MAX}	ΔA_{MAX}	D_A $[(\Delta D_A)_{MAX}]$	D_B $[(\Delta D_B)_{MAX}]$
CB[9]	0.0013	4.1°	1.36 [0.20]	1.34 [0.05]
C60	0.0005	1.1°	0.71 [0.0035]	0.71 [0.0035]

Table S1: Values PM6 for the maximum variation of bond length ΔR_{MAX} (in nm), maximum variation of angles ΔA_{MAX}, average diameter D_A and D_B and respective maximum variations $(\Delta D)_{MAX}$ (in nm) for C_{60}@CB[9] complex. All results was obtained in dissociation process of C_{60}@CB[9] complex, where the centers of mass R_{CM} of each monomer was separated by 0.02 nm in a range of 0.98 nm.

Figure S3 shows this behavior as a function of distance. We can see that during inclusion, as the diameter widens (reaching its maximum value at the center-of-mass distance of 0.25 nm) is the diameter DB shortens, about the same distance.

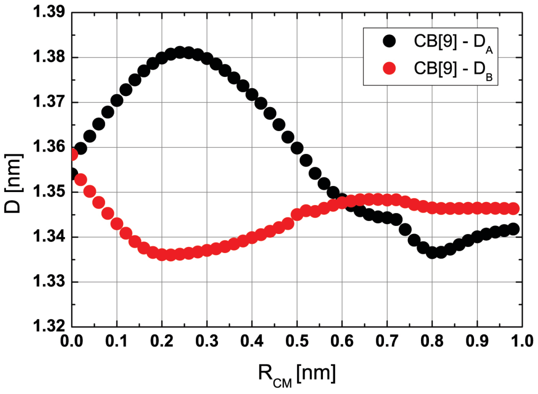

Figure S3: PM6 values of the average diameter D_A e D_B (in nm) of the CB[9]. The centers of mass R_{CM} of each monomer were separated by 0.02 nm in a range of 0.98 nm.

2.2 - Electronic Properties

As discussed in the main text, the approaching of the C_{60} to the CB[9] oxygen portals, results in a marked change of the electron cloud of the fullerene. Another indicator for this effect (beyond the induced dipole, already discussed) is the induced charge on the carbon cage. In Figure S4 we selected some atoms in different regions of C_{60} and plot the value of its charges in function of the monomers center-of-mass separation. We can see, for instance, the equatorial carbons are those with the greatest charger variation, ranging from -0.06e to +0.06e and depending on the position.

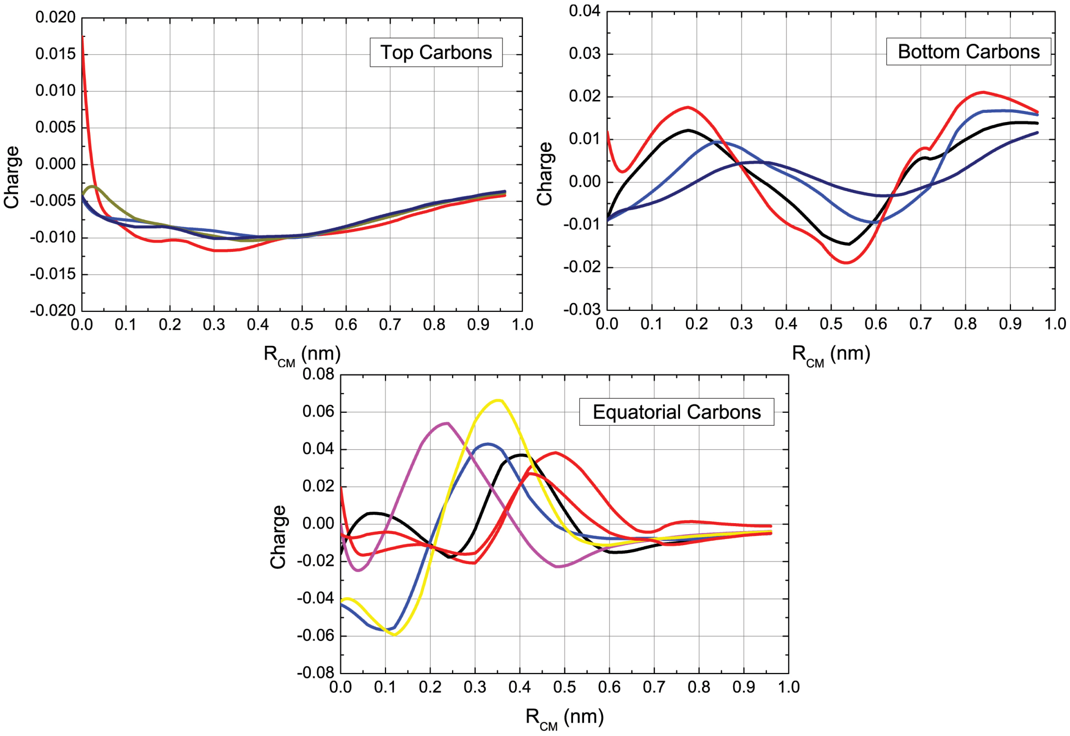

Figure S4: Variation of the ωB97X-D/6-31G(d,p) Mulliken atomic charges (in elementary unit, *e*) for selected carbon atoms of C_{60}. All results were obtained for the inclusion process of C_{60} into CB[9]. The center of mass distance, R_{CM}, was incremented by 0.02 nm for a range of 0.98 nm.

Another indicator to the changes in the electron cloud of the fullerene when its approaches to the hydrophilic CB[9] is showed at Figure S5. The wB97X-D/6-31G(d,p) results for the Mulliken atomic charges shows that there is charge transfer between the monomers during the inclusion process.

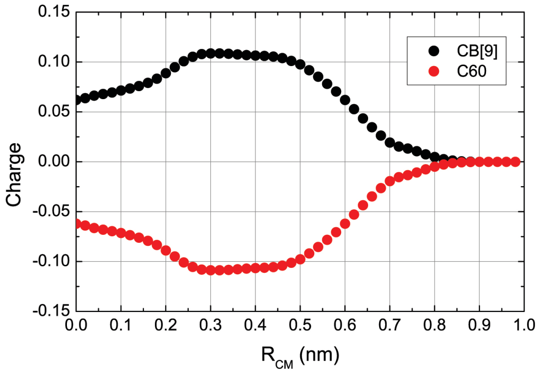

Figure S4: Variation of the ωB97X-D/6-31G(d,p) Mulliken atomic charges (in elementary unit, *e*) versus the distance between the center of mass of C_{60} and CB[9] during the inclusion process of C_{60} into CB[9]. The center of mass distance, R_{CM}, was incremented by 0.02 nm for a range of 0.98 nm.

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