Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Electronic Supplementary Information

## 1 Molecular systems

The homogeneous system is composed by one β-cyclodextrin and one ferrocenemethanol in a 3000 water molecules aqueous phase. The solubility of Fc being low in aqueous solution, the simulations were performed using ferrocenemethanol. The heterogeneous system consists of a per-6-thio-β-cyclodextrin grafted on a five layers of Au(111) surface through 7 grafted points (one on each glycosidic unit). The grafted points on the surface were selected so that the angle between the carbon, sulfur and gold atoms was the closest to the equilibrium angle value used in the forcefield. The gold surface is composed of layers of $13\times16$ fcc lattice, so that the dimensions of the simulation box along the $x$ and $y$ axes are 37.4 Å and 39.9 Å, respectively. As the system is non-periodic along the direction normal to the surface ($z$-axis), the simulation cell is closed by an additional gold layer. The separation distance between the two surfaces was fixed to 46.8 Å which is large enough for the water molecules to recover a bulk behavior in the middle of the cell. The simulation box is then elongated along the $z$-direction with empty spaces, up to 280 Å, in order to apply a three dimensional scheme for the calculation of the electrostatic interactions[1,2]. In order to satisfy an accurate bulk density for water, the space between the two surfaces is filled by 2000 water molecules.

## 2 Interaction model

The intramolecular and intermolecular interactions were described by the CHARMM forcefield[3–5]. The Au parameters were taken from the work of Ayappa and coworkers[6]. The ferrocene part was modeled by the parameters described by de Hatten *et al*[5]. The water molecules were represented by the TIP4P/2005 model[7]. The partial charges of the β-cyclodextrin were calculated from the density functional theory (DFT)[8,9] (B3LYP)[10,11] with effective core potential (SD-DALL) Gaussian basis using the Gaussian 03 package[12] and the CHELPG[13] procedure as a grid-based method. The repulsion-dispersion interactions were described using the Lennard-Jones (LJ) potential. The LJ potential parameters between unlike atoms were calculated with Lorentz-Berthelot mixing rules. The electrostatic interactions were calculated with the three dimensional Smooth Particle Mesh Ewald (SPME) method[14].

## 3 Simulation details

MD simulations were run in the constant-NPT statistical ensemble using Hoover thermostat and barostat[15,16] with relaxation times of 1 ps and 5 ps, respectively. The equations of motion were integrated using the Verlet leapfrog algorithm scheme at T=298 K and P=1 atm with a timestep equal to 2 fs. The C-H covalent bonds were kept of fixed length by using the SHAKE algorithm[17]. The cutoff radius for the Lennard-Jones interactions and for the real part of the electrostatic interactions was chosen to 16 Å. The convergence parameter for the SPME summation was fixed to 0.1960 $Å^{-1}$. The reciprocal space for the SPME method was developed on a number of $k$-vectors equals to 8, 8 and 64, along $x$-, $y$- and $z$-direction, respectively. With these parameters the calculation of the electrostatic interactions satisfies a relative error of $10^{-6}$. Simulations were performed using the parallel version of the modified DL_POLY_MD package[18] using up to 12 processors at a time. The potential of mean force (PMF) was calculated by the Thermodynamic Integration method. The perturbed quantity was the distance between the centers of mass of the CD and Fc molecules. The distance between the two molecules was constrained with the SHAKE algorithm. One simulation was performed each 0.05 Å and each typical simulation run of the system consisted of an equilibrium period of 200 ps and a production phase of 400 ps. For example in the free CD system, the simulation time to get the total PMF curve is 162.6 ns which would represent 6.2 CPU years on a single processor.

## 4 Thermodynamic properties

The thermodynamic quantities were obtained by integrating the PMF profile along the separation distance between CD and Fc[19,20] considering a cylindrical approach[21,22]. Indeed, when the Fc enter into the CD cavity, the Fc accessible volume is restrained to a small cylinder defined by the area available for its in-plane movement (perpendicular to the CD axis). The mean radius of that cylinder was evaluated from the trajectory of the center of mass of the Fc at each CD-Fc separation distance. For the surface-confined CD case, the potential of mean force was integrated from the largest separation distance (for which there is no interaction between the two molecules) to that for which the repulsion is maximum. As concerns free CD, the integration was

calculated from each side of the PMF curve (where CD and Fc have no interaction) to the central maximum (separation distance of 0.4 Å) and the thermodynamic properties were averaged over these two reaction pathways.

## 5 Structural parameters

We have calculated structural parameters for Fc and CD before and after the association in both homogeneous and heterogeneous systems. Since Fc has few internal degrees of freedom, its contribution to the entropy change is only related to its global motion of translation and rotation. To investigate this parameter, we have plotted the distribution of the angle between the CD axis and the Fc axis (Figure S1). The width of the distribution is evaluated by the value of $\Delta\theta$ reported on Figure S1 and defined as twice the standard deviation. We observe that the relative motion between Fc and CD is more important for the free CD, with a larger distribution. Since Fc penetrates less deeply into the free CD cavity, it oscillates and keeps a relative mobility. On the contrary, the deeper insertion of the Fc into the surface-confined CD implies a significant loss of degrees of freedom as shown by the narrower distribution.

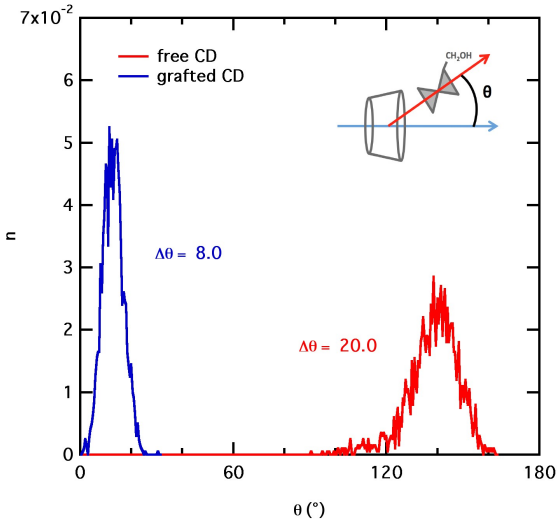


**Figure S1** Distributions of the angle θ between CD axis and Fc axis. The angle is defined in the inset. $\Delta\theta$ represents the width of the distribution and is equal to twice the standard deviation.

The deformation of the CD is investigated through the distributions of the squared value of the radius of gyration of the molecule (see Figure S2). For free CD, no significant change is observed in the distributions (Figure S2 a). This means that the repartition of the mass of the CD is not modified by the association with Fc. Concerning the surface-confined CD (Figure S2 b), the $Rg^2$ value is slightly increased in the case of the formation of the complex. However, we observe that the width of the distribution is unchanged, the standard deviation being equal to 0.3 Å for both distributions. The larger $Rg^2$ value for the grafted CD, can be easily explained by the insertion of the Fc into the CD cavity. The fact that the width of the distribution is identical reveals no significant difference as regards the mobility of the CD. Finally, these results indicate that the association with Fc does not change strongly the structure of the CD in both homogeneous and heterogeneous systems.

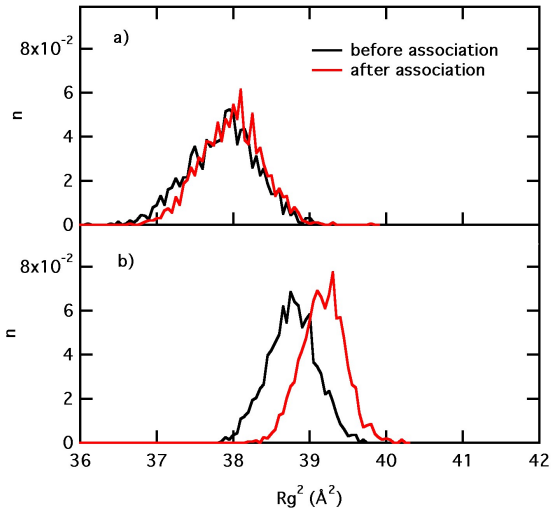


**Figure S2** Distributions of the squared value of the CD radius of gyration in a) homogeneous system and b) heterogeneous system before and after association.

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