

Supporting information

Computational Details – Creation and Simulation of the Molecular System

The starting model of a portion of dendrimer fiber pre-equilibrated in water used in this work was taken from our previous study explaining in detail the mechanism of formation of the PPI[G4]-Cd(CH₃COO)₂ fibers.^{S11} The molecular model is composed of two G4 PPI dendrimers which surface amino groups are partially coordinated by Cd²⁺ ions from dissolved Cd(CH₃COO)₂ – 10 Cd²⁺ for each dendrimer, according to the experimental stoichiometry of 1:10 (PPI[G4]:Cd(CH₃COO)₂). In the experimental condition, 10 amino groups of each PPI dendrimer over the total 32 are coordinated with Cd²⁺ ions, while the remaining 22 are protonated (NH₃⁺) and carry a +1e charge each (the total charge present on each dendrimer coordinated with Cd²⁺ ions is +42e). Our previous molecular dynamics (MD) simulations demonstrated that, despite the high positive charge present on each PPI dendrimer, the AcO⁻ ions coordinate to the Cd²⁺, and work as “ionic glue” at the interface between the dendrimers stabilizing the fiber (**D1+D2-AcO⁻**).^{S11}

The modeling work was conducted with the AMBER 11 suite of programs.^{S12} The residues that compose the dendrimers, the AcO⁻ ions and the SH⁻ ions were parametrized according to the “general AMBER force field (GAFF)” (*gaff.dat*),^{S11,S13} consistent with a validated procedure adopted by our group in previous studies on dendrimers^{S14} and dendrons.^{S15} The partial charges for all residues were obtained using the AM1-BCC^{S16} calculation method within the *antechamber*^{S17} module of AMBER 11.^{S11} Parameters for the Cd²⁺ ions consistent with the AMBER force field were taken from recent literature.^{S18}

The molecular model for the fiber portion (**D1+D2-AcO⁻**) was solvated in a periodic box containing TIP3P^{S19} water molecules extending 20 Å from the solute atoms. In the experiments, a molar ratio of 1:2 Na₂S:Cd²⁺ (and thus of SH⁻:Cd²⁺) was used. Consistently, a total of 10 SH⁻ ions (5 SH⁻ ions for each PPI dendrimer) and 10 Na⁺ from dissolved Sodium Sulfide (Na₂S) were added

in the system using the *leap* module within AMBER 11. In particular, the ions were added in the periodic systems around the initial pre-equilibrated configuration of the **D1+D2**-AcO⁻ fiber with the standard *addIons* utility of *leap* (AMBER 11). Ions were placed onto a shell around the solute using a Coulombic potential on a grid (water molecules were replaced with ions if eventual superposition occurred).

The system containing the pre-equilibrated **D1+D2**-AcO⁻ complex^{S11} in aqueous solution with SH⁻ and Na⁺ ions (Figure S11) was initially minimized and then two preliminary steps of molecular dynamics (MD) simulations were run for 50 ps in NVT (constant N: number of atoms, V: volume, T: temperature) and NPT (constant N: number of atoms, P: pressure, T: temperature) conditions respectively to reach the simulation temperature of 300 K and to relax the density of the solvent inside the periodic box. During these two preliminary simulations the dendrimers were blocked while ions and solvent molecules were let free to move. After these initial steps, any restraint was removed and the system underwent 100 nanoseconds (ns) of MD simulation in NPT (constant N: number of atoms, P: pressure and T: temperature) periodic boundary condition at 300 K of temperature and 1 atm of pressure. A time step of 2 femtoseconds, the Langevin thermostat and a 10 Å cutoff during the MD runs. The particle mesh Ewald^{S110} (PME) approach was used to treat the long-range electrostatic interactions and all bonds involving Hydrogen atoms were treated according to the SHAKE algorithm.^{S111}

During the MD simulation, many SH⁻ replace AcO⁻ ions in close proximity of the Cd²⁺ ions (Figure S11 and enclosed MD movie). The affinity energy (ΔE_{attr}) of SH⁻ and AcO⁻ ions for Cd²⁺ was extracted from the molecular dynamic (MD) simulations and calculated over 200 of snapshots taken from the equilibrated phase of the MD trajectories using the MM-PBSA approach.^{S11,S112} The ΔE_{attr} values reported in Figure S1 demonstrate that ionic substitution in correspondence of the Cd²⁺ ions is due to the affinity of SH⁻ ions for Cd²⁺ which is higher than that of AcO⁻ ions.

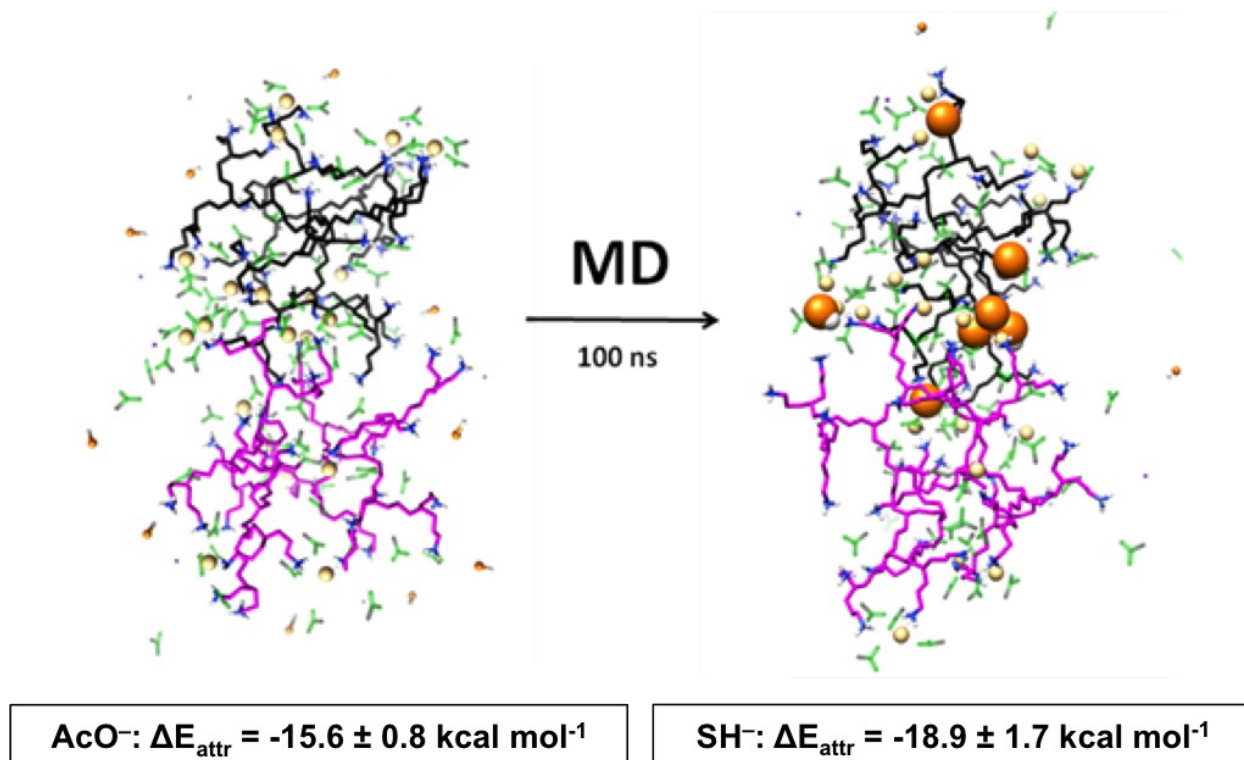


Figure S11. Snapshots taken from the MD simulation of the **D1+D2-AcO⁻** + 10 SH⁻ - (orange) and 10 Na⁺ (purple). Notably, after 100 ns many SH⁻ ions (7 over a total of 10 in the system) form a stable coordination with Cd²⁺ (orange large spheres) through ionic-substitution of AcO⁻ ions (a movie of this simulation is also provided). These ionic interactions are responsible of the *in situ* formation of CdS domains along the fiber.

Table S11. The main features of the simulated molecular system

Complex	Number of Cd ²⁺ ^[a]	Number of AcO ⁻ ions in the system ^[b]	Number of SH ⁻ added in the system ^[c]	Number of Na ⁺ added in the system ^[d]	Box volume (Å ³)	Number of water molecules in the system	Total number of atoms in the system
D1+D2-AcO⁻ ^[e]	20	84	0	0	474306	14564	45700
D1+D2-AcO⁻+10SH⁻+10Na⁺	20	84	10	10	580444	15145	47473

^[a] Experimental ratio of 1:10 between PPI dendrimers and Cd²⁺ ions. ^[b] Total number of AcO⁻ ions inserted in the system consistent with the 1:10 PPI: Cd(CH₃COO)₂ experimental concentration and to guarantee overall systems neutrality. ^[c] Total number of SH⁻ ions added in the system (experimental 1:5 PPI:SH⁻). ^[d] Number of Na⁺ added in the system consistently with the experiments from dissolved Na₂S ((experimental 1:5 PPI: Na₂S). ^[e] Data taken from our previous work explaining the mechanism of fibers formation.^{S11}

Radial distribution function (RDF) plots and surface cadmium sulphide formation

The equilibrated MD trajectories were processed with the *ptraj* module of AMBER 11 in order to obtain the radial distribution functions (RDF) of Cd²⁺, AcO⁻ and 10 SH⁻ ions which are useful to study the stability of the coordination between AcO⁻ and SH⁻ ions with the surface of the dendrimer (Figure SI2). RDF represents density distribution of these ions in space with respect to a reference point (the center of mass of the dendrimer **D** in Figure S1a, or the Cd²⁺ ions in Figure S1b). This gives indication about the presence of Cd²⁺, AcO⁻ and SH⁻ ions in a certain zone of the system (spatial density) during the simulation. In RDF, high and narrow peaks identify high density of atoms in a certain zone, but also high localization and low mobility of the atoms (stable localization). On the other hand, broad and low intensity peaks indicate low density and high mobility. Importantly, peaks superposition between the Cd²⁺ and AcO⁻ and SH⁻ curves indicates that the interactions between AcO⁻ and SH⁻ with the surface Cd²⁺ ions are stable and persistent over the MD simulation.

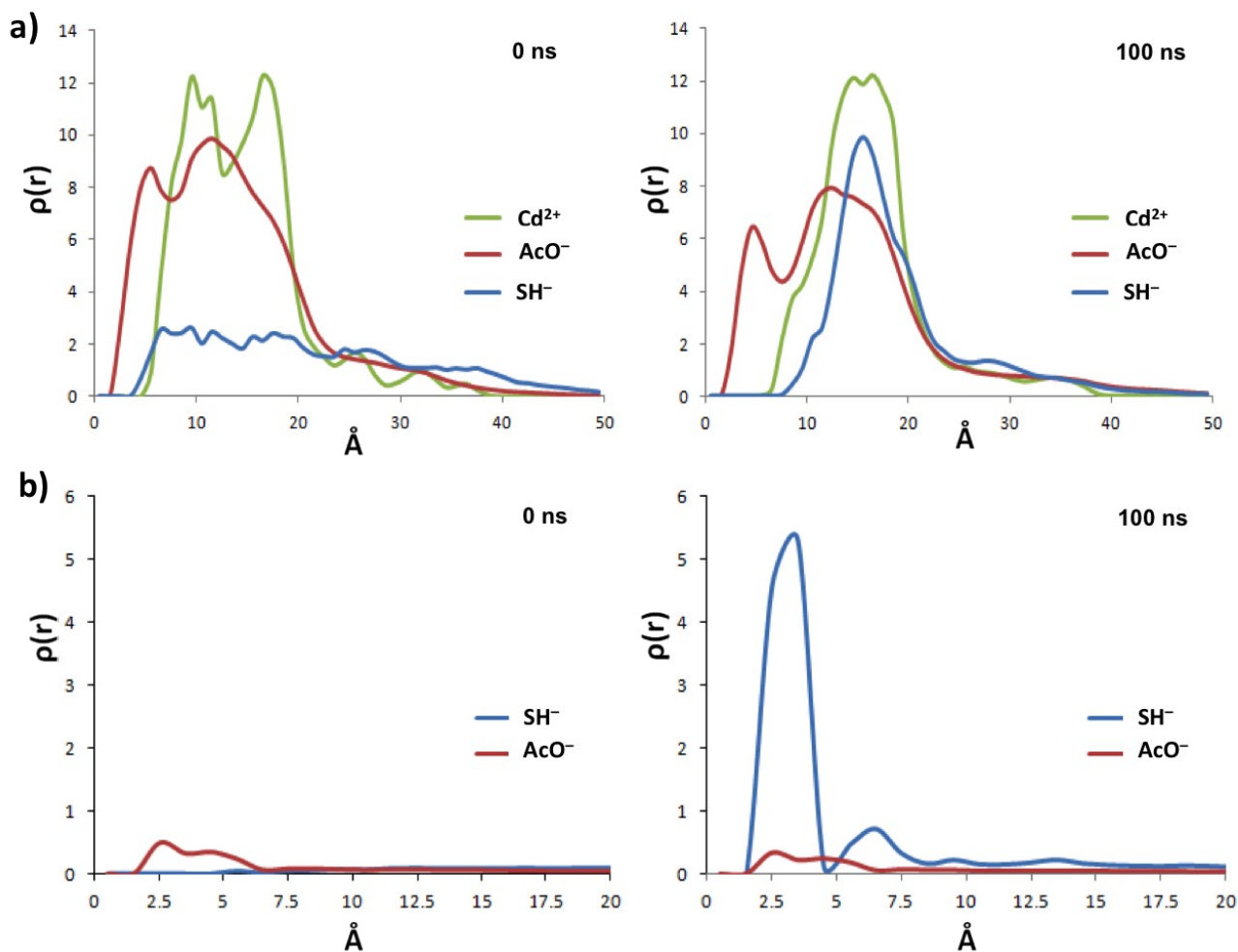


Figure S2. Radial distribution functions (RDF) profiles of Cd²⁺, AcO⁻ and SH⁻ ions. (a,b) Situation at the start of the simulation (0 ns) with ions dispersed in the simulation box (left), and after 100 ns of MD simulation (right). (a) RDF of Cd²⁺ (green), AcO⁻ (red) and SH⁻ ions (blue) respect to the distance (in Å) from the center of mass of the dendrimer. Peaks superposition indicates that the ions oscillate at the same distance of Cd²⁺ from the dendrimer's center. We note that after 100ns many (7 over a total of 10) SH⁻ ions oscillate stably near Cd²⁺. (b) RDFs of SH⁻ and AcO⁻ ions calculated respect to Cd²⁺ (origin of the x axis). At the end of the MD simulation most of SH⁻ ions are at a stable distance from Cd²⁺ ions (stable coordination), which is evidence of AcO⁻ ion substitution.

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