Electronic Supplementary Information

Self-assembly of Porphyrin-DNA Hybrids into Large Flat Nanostructures

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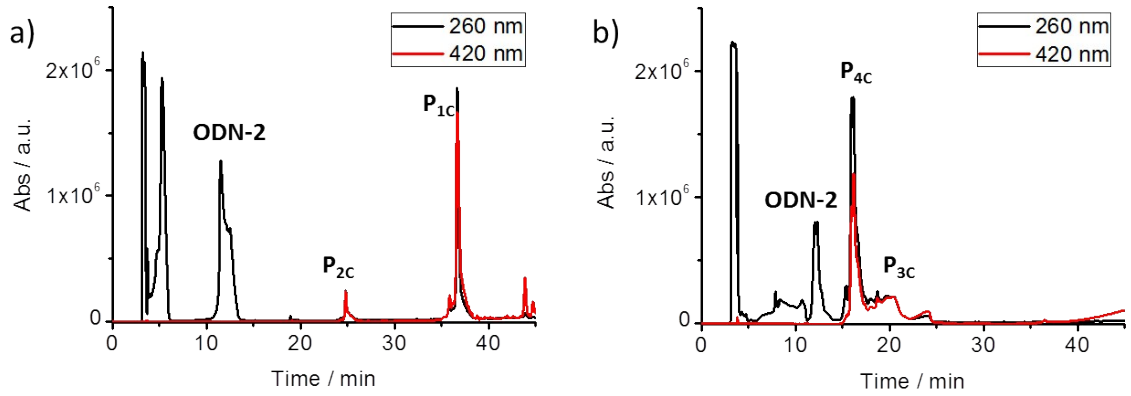

Fig. S1 RP-HPLC chromatograms recorded at 260 nm (black) and 420 nm (red) after the first step (a) and the second step (b) of the reaction between porphyrin **1** and **ODN-2**. The chromatograms show the formation of $\mathbf{P_{1C}}$ with traces of $\mathbf{P_{2C}}$ during the first step (a) and its conversion into $\mathbf{P_{3C}}$ and $\mathbf{P_{4C}}$ after the second step (b).

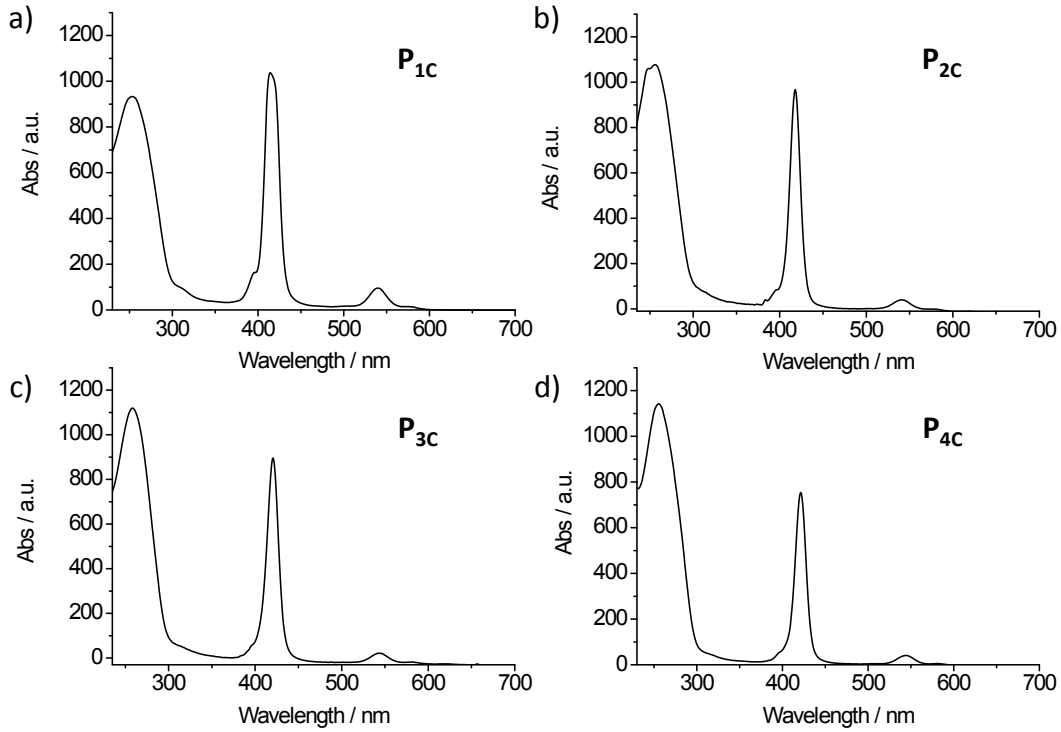

Fig. S2 UV-Vis absorption spectra of the porphyrin/ODN mono-, bis-, tris- and tetra-adducts (**P_{1C}**, **P_{2C}**, **P_{3C}** and **P_{4C}**) recorded between 220 and 700 nm. Similarly to **P_n** (n=1 to 4) series, the relative contribution of the porphyrin absorption (Soret band at 420 nm) decrease when more oligonucleotides are attached.

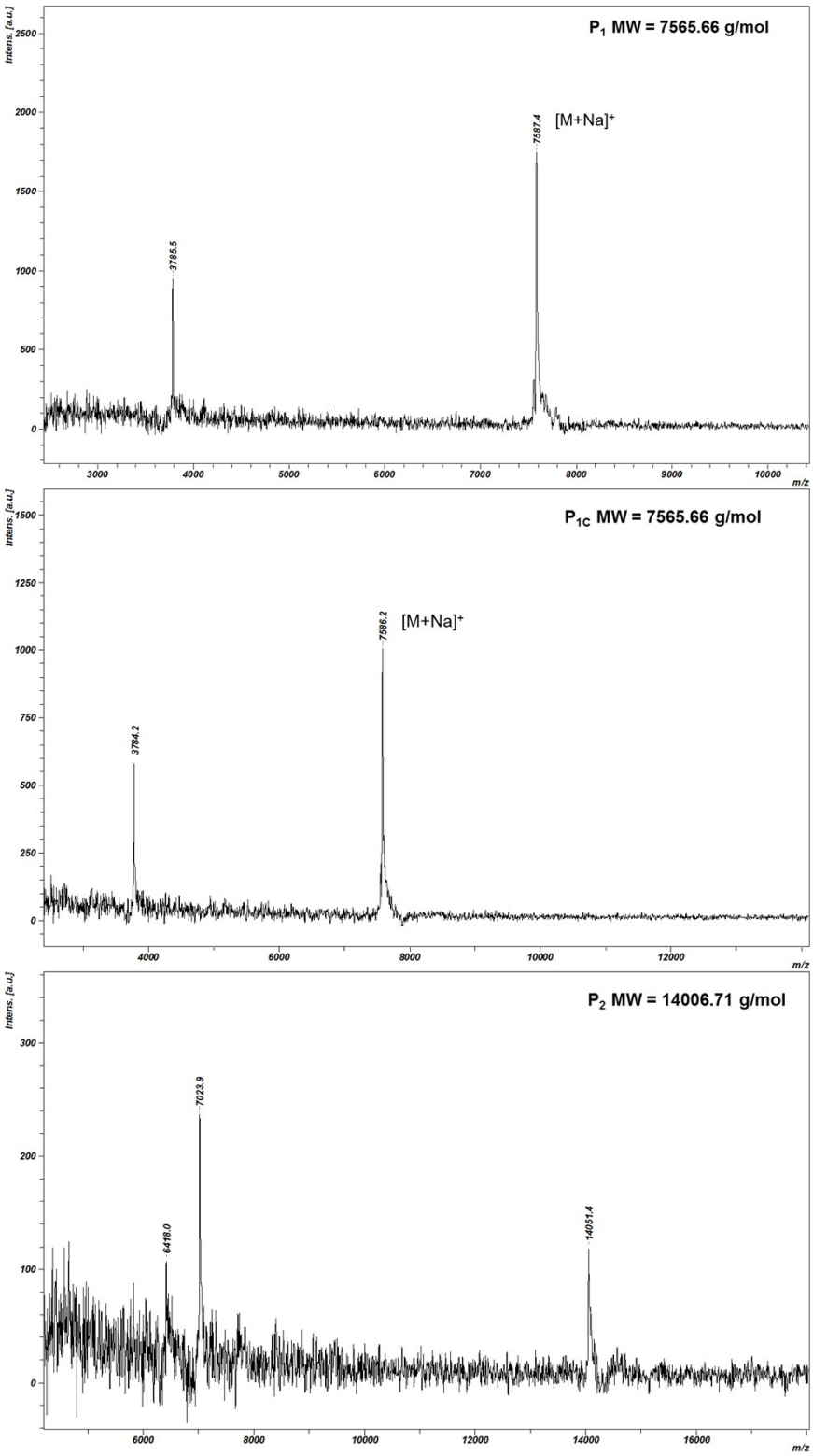

Fig. S3 MALDI-TOF mass spectra of $\mathbf{P_1}$, $\mathbf{P_{1C}}$ and $\mathbf{P_2}$. It was impossible with our equipment to analyze oligonucleotides with size bigger that 20 kDa because of loss of resolution and sensitivity due to the presence of salts (Na^+, K^+ adducts) and therefore we were not able to obtain the mass spectrum of $\mathbf{P_{2C}}$, $\mathbf{P_3}$, $\mathbf{P_{3C}}$, $\mathbf{P_4}$, and $\mathbf{P_{4C}}$.

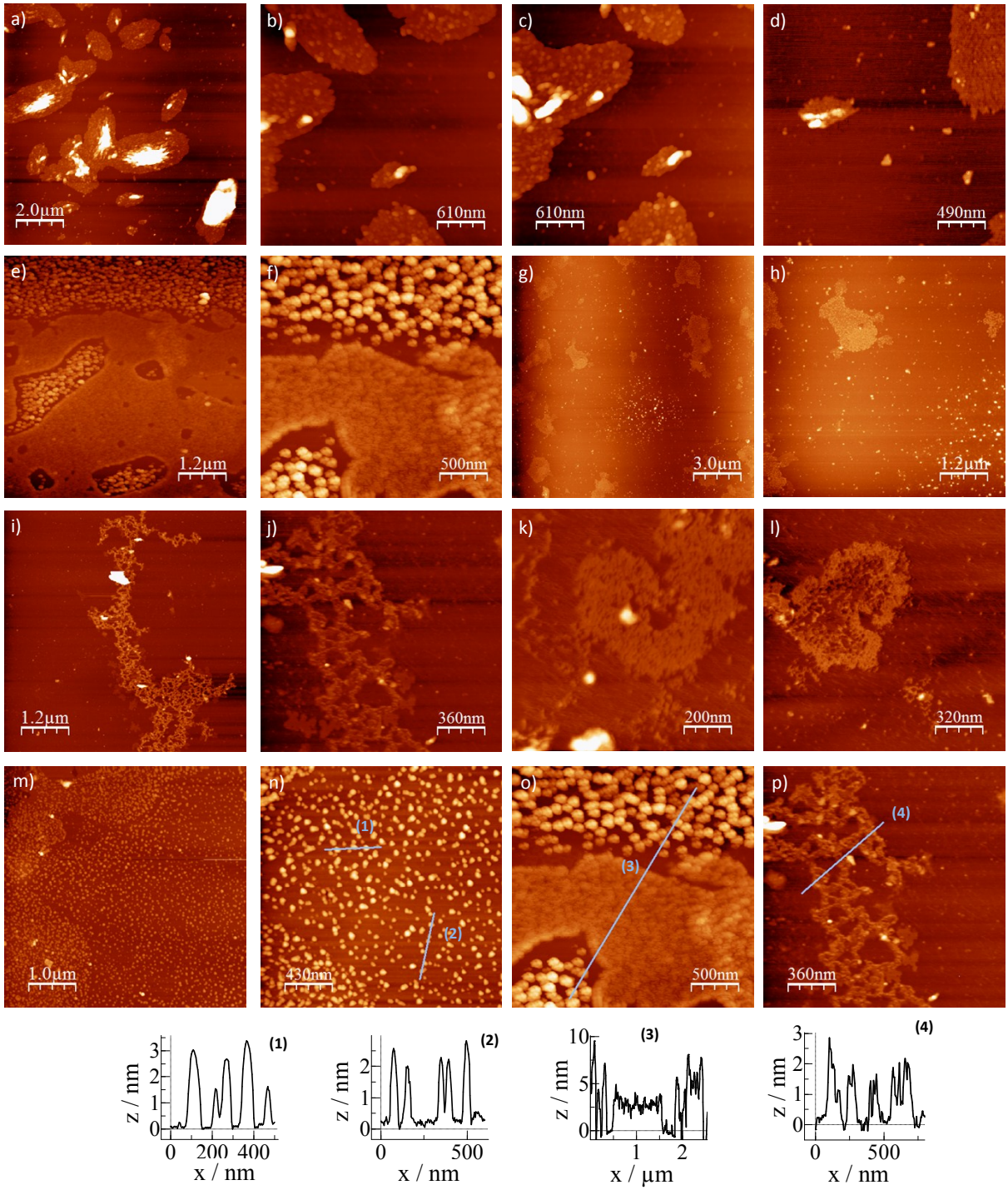

Fig. S4 Additional AFM images of **P_4 / P_{4C}** nanostructures on mica. Images (a-d): additional images of the structures observed on the same substrate as Fig. 4. Images (e-h): example of structures obtained on another mica substrate prepared under the same conditions; on images (e) and (f), one can clearly see the coexistence of flat structures and round-shape aggregates. Images (i-l): example of structures obtained for a substrate on which the buffer

evaporated totally during the annealing. This series of images show wire-type aggregates and non-uniform islands of DNA hybrids. On this last substrate, the 2-dimensional structures did not form properly probably because the sample dried during annealing. It is interesting to note that Fig. S3k-l show structures that are similar to the ones observed on Fig. S3a-h but these structures are incomplete. It may give indications on the growth mechanism: some DNA islands are formed on the surface and as the temperature decreases some DNA hybrids from the solution are captured and participate to the growth of the 2D structures. Images (m-n): images and cross-section analysis of structures obtained when the mica substrate is directly immersed in the $\mathbf{P_4}$ / $\mathbf{P_{4C}}$ hybrid solution; in this case no flat structures are obtained and only round shape aggregates if *ca.* 2-3 nm of diameter are observed. Image (o): cross-section analysis of image (f); the round-shape aggregates show bigger height than the 2D flat structure. It supports the assumption that the 2D nanostructures are formed on surface probably from the decomposition of the round-shape aggregates. Image (p): cross-section analysis of a zoom of image (i); the image show fibril-like structure of *ca.* 2 nm in height.

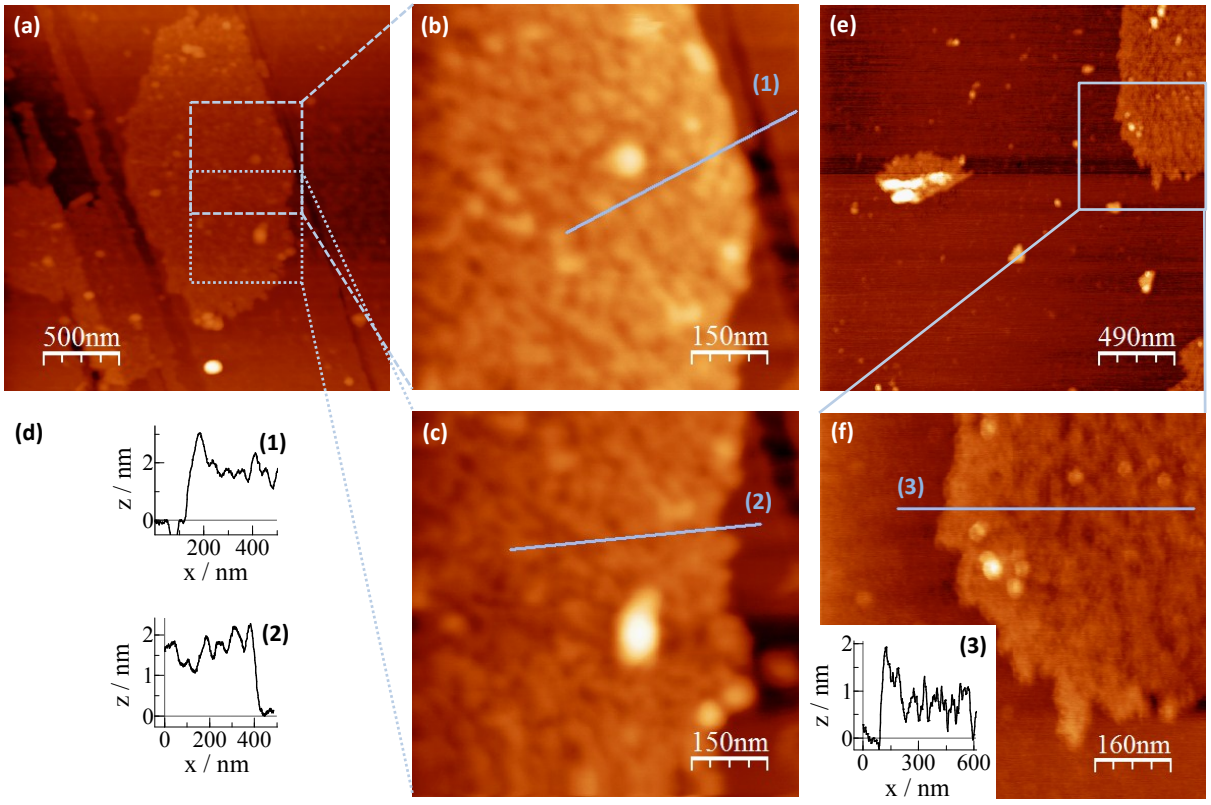

Fig. S5 (a) and (e) example of images of the porphyrin/DNA nanostructures. (b), (c), (d) and (f) images showing the details of the flat structures and their cross-section analyses; compared to the round-shape aggregates visible in several cases (Fig. S4), the 2D structures are formed by fibril-like aggregates which suggests that these structures are not formed simply by clustering of the round-shape aggregates but rather by the coalescence and the rehybridation of these aggregates into flat nanostructures.