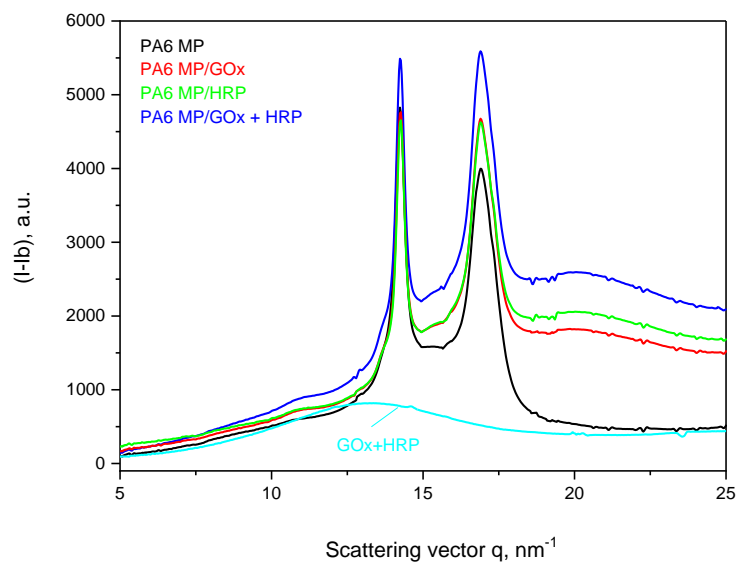


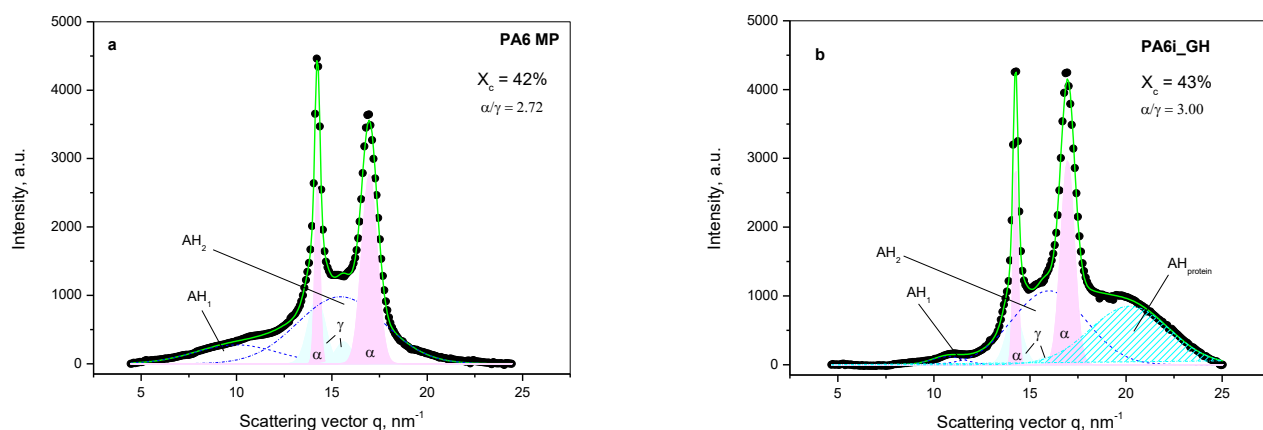
**Figure S1.** Chemical reactions occurring during AAROP of  $\epsilon$ -caprolactam to PA6 MP. The chemical structure of the C20 imide activator and of the AAROP initiator dicaprolactamato-bis-(2-methoxyethoxy)-aluminate (DL) are also opresented.

**Table S1.** Elemental analysis of PANF samples by SEM/EDX with ZAF corrections.

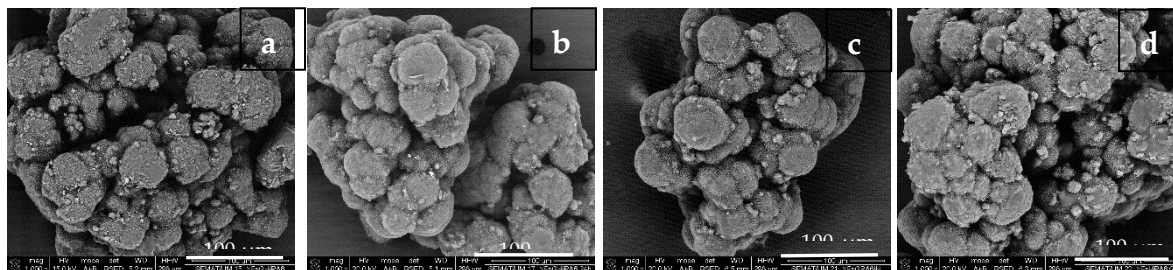
Element, wt. %	Sample denomination							
	NF GH/PA		NF GH&PA		NF G/PAiH		NF G&PAiH	
	ZNF	ZPA6	ZNF	ZPA6	ZNF	ZPA6	ZNF	ZPA6
Cu K	32.2	2.5	35.5	2.3	30.4	0.0	27.4	2.5
P K	11.5	1.2	11.6	1.3	9.5	1.4	9.3	1.8



**Figure S2.** WAXS linear profiles of PA6 MP support before and after adsorption immobilization of GOx, HRP or GOx+HRP. The diffuse amorphous peak of the GOx+HRP mixture is also presented.



**Figure S3.** Deconvolution of the WAXS linear profiles of PA6 MP support before (a) and after (b) adsorption immobilization of GOx+HRP dyad. The new amorphous  $AH_{protein}$  peak at  $q = 20.2 \text{ nm}^{-1}$  found in the latter case is due to the H-bond formation of the absorbed enzymes with the support amorphous phase. Comparing the srystalline structure of PA6 MP and PA6\_GH shows no changes in the support crystalline structure after enzyme absorption immobilization: the crystallinity index  $X_c$  and the  $\alpha/\gamma$  polymorph relation remain quite similar, the differences being in the margin of the experimental error of the WAXS method.



**Figure S4.** SEM micrographs of polymer-assisted hybrid nanoflowers (PANF) after the 6th catalytic cycle: (a) - NF GH/PA; (b) - NF GH&PA; (c) NF G/PAiH; (d) NG G&PAiH. The brighter dot areas contain residual NaCl from the PBS or  $\text{Cu}_3(\text{PO}_4)_2$  from the NF. For more details, see the main text.