Electronic Supplementary Information

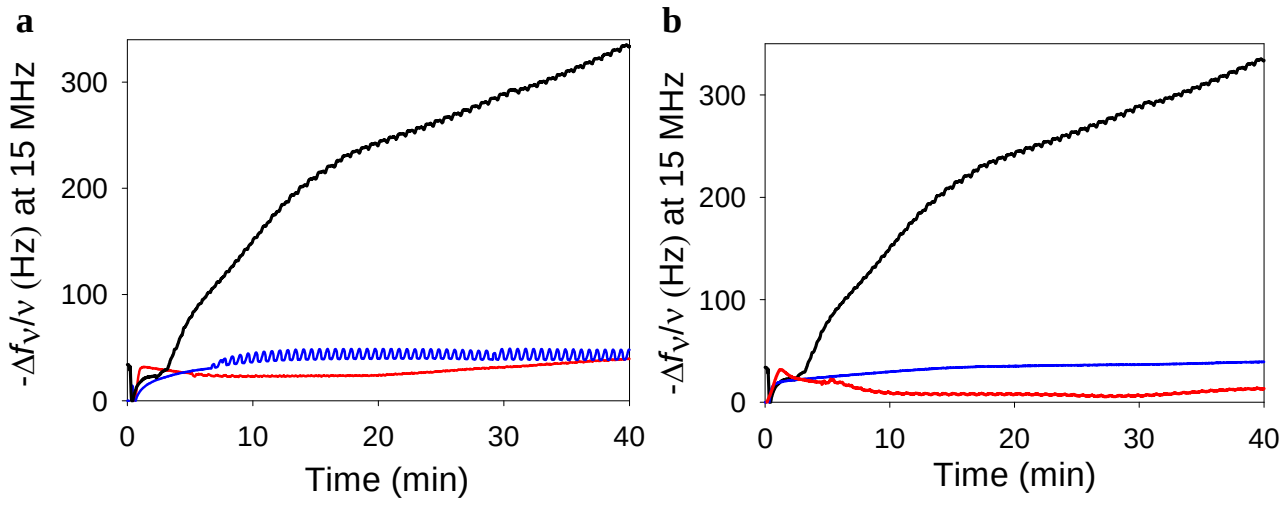

Fig. S1 (**a)** Evolution of the opposite of the normalized frequency shift, measured at 15 MHz (ν = 3) by EC-QCM, in the presence of a ($PAAN_3$, C≡C-CD, C≡C-Fc) mixture (black line), a ($PAAN_3$, C≡C-Fc) mixture (blue line), and a ($PAAN_3$, C≡C-CD) mixture (red line) with 0.6 mM $CuSO_4$ prepared in 50% (v/v) ethanol-water solution during the application of CV between -350 mV and +750 mV (vs. Ag/AgCl, scan rate of 50 mV/s). **(b)** Evolution of the opposite of the normalized frequency shift, measured at 15 MHz (ν = 3) by EC-QCM, in the presence of a ($PAAN_3$, C≡C-CD, C≡C-Fc) mixture with 0.6 mM $CuSO_4$ prepared in 50% (v/v) ethanol-water solution (black line), without 0.6 mM $CuSO_4$ (blue line) during the application of CV between -350 mV and +750 mV (vs. Ag/AgCl, scan rate of 50 mV/s) and without application of any potential (red line). The frequency shift increase observed in the first minutes corresponds to the adsorption of the functionalized PAA on the PEI pre-coated surface. Small oscillations which superimpose the continuous increase are due to the cyclic electrochemical formation and dissolution of a Cu(0) layer.

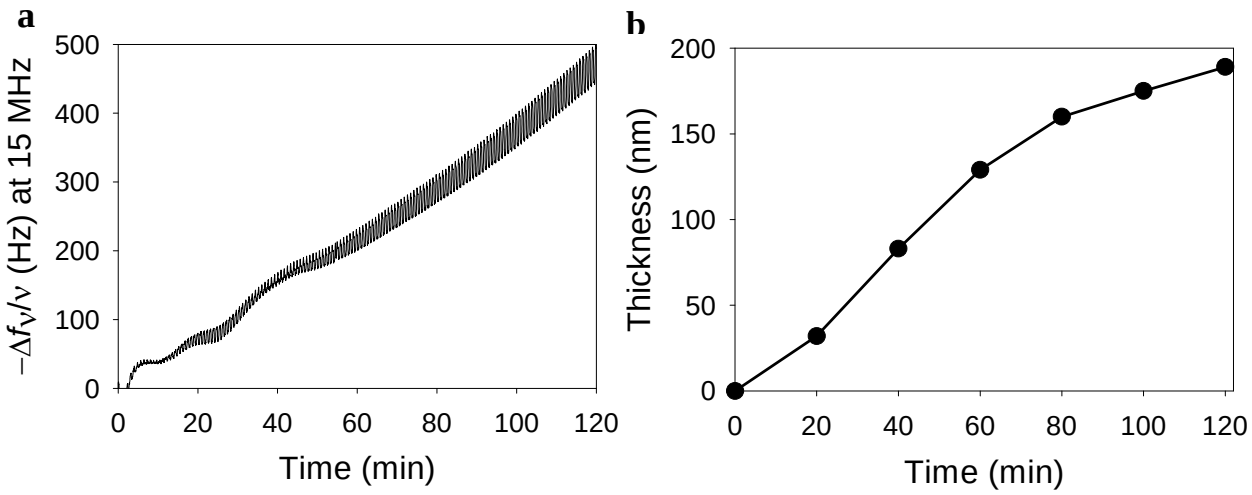

Fig. S2 (a) Evolution of the opposite of the normalized frequency shift of ($PAAN_3$, C≡C-Ad, C≡C-CD) mixture as a function of time, measured at 15 MHz (ν = 3) by EC-QCM and **(b)** the corresponding calculated thickness during the application of CV between -350 mV and +750 mV (vs. Ag/AgCl, scan rate of 50 mV/s). The ($PAAN_3$, C≡C-Ad, C≡C-CD) mixture was prepared at concentrations of 10^{-4} M for azide groups and 2×10^{-3} M for alkyne (with [C≡C-Ad] = [C≡C-CD]) in the presence of 0.6 mM $CuSO_4$ prepared in 50% (v/v) ethanol-water solution. The film is built on a PEI pre-coated surface. The film thickness is calculated using the Voigt model[31] applied to the EC-QCM data and subtracting the contribution of the electrostatic adsorption on PEI.

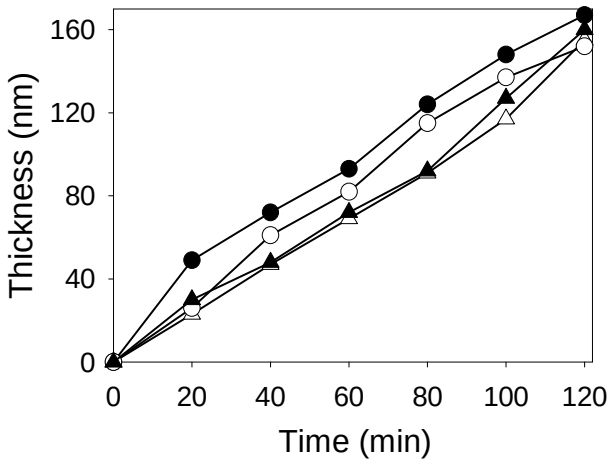

Fig. S3 Evolution of the thickness of ($PAAN_3$, C≡C-CD, C≡C-Fc) films as a function of time during the application of CV between -350 mV and +750 mV (vs. Ag/AgCl, scan rate of 50 mV/s) obtained with ($PAAN_3$, C≡C-CD, C≡C-Fc) mixture prepared with 0.6 mM $CuSO_4$ in 50% (v/v) ethanol-water solution for [C≡C-Fc] of 100 % (●), 75 % (▼) 50 % (○), 25 % (▲) of its standard value (10^{-3} M). The film is built on a PEI pre-coated surface. The film thickness is calculated using the Voigt model applied to the EC-QCM data and subtracting the contribution of the electrostatic adsorption on PEI.

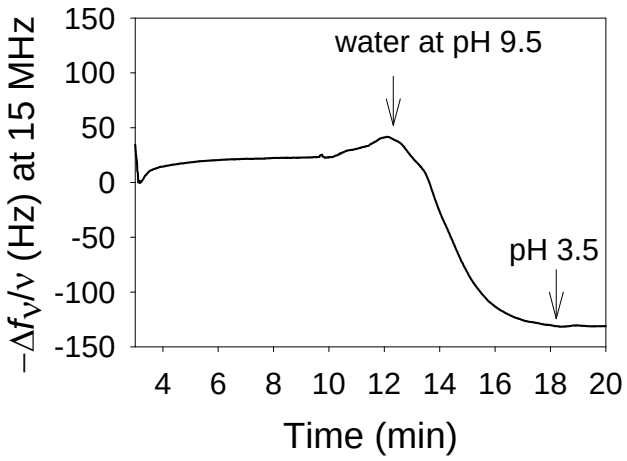

Fig. S4 Evolution of the opposite of the normalized frequency shift as a function of time, measured at 15 MHz (ν = 3) by EC-QCM, during the contact of a self-constructed ($PAAN_3$, C≡C-CD, C≡C-Ad) film with water solutions at pH 3.5 and 9.5 under 0.1 mL/min flux. The film thickness is calculated using the Voigt model applied to the EC-QCM data and subtracting the contribution of the electrostatic adsorption on PEI. The contact of the film with a pH 9.5 solution induces the reduction of the film thickness from 67 nm down to 16 nm.