Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supplementary Informations

Promotion of sugar - lectin recognition through multiple sugar presentation offered by Regioselectively Addressable Functionalized Templates (RAFT): a QCM-D and SPR study

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Characterization of the grafting of thiolated RAFT ligands on gold surfaces

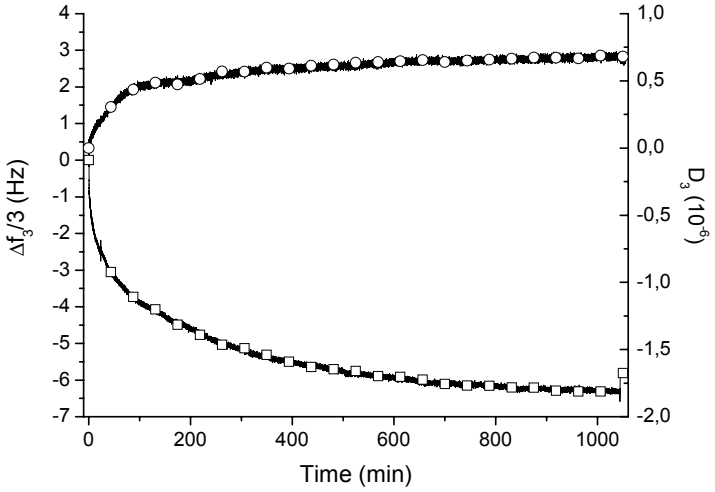

Fig. ESI-1. QCM-D responses, normalized frequency shift Δfn/n ( ) and energy dissipation Dn (○) for the third overtones (n=3), recorded during the grafting of thiolated RAFT-$(Man)_1$ (0.1 M in water) on a gold coated QCM-D transducer.

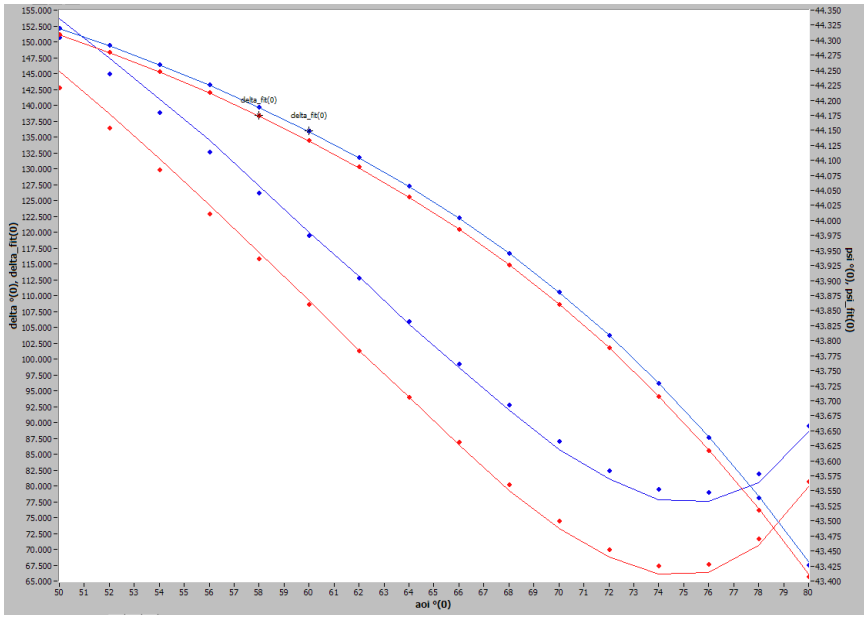

Fig. ESI-2. Ellipsometric measurements: Experimental Δ and ψ values (lines) and best fits (points) as a function of incidence angle measured on the bare gold substrate (blue) and RAFT modified substrate (red). The optical properties of substrate were fitted using a two-phase model (substrate/ambient air) and gave the following values: $n_s = 0.201 \pm 0.011$; $k_s = 3.611 \pm 0.011$ (mse = 0.97). These values were used to fit the data of 20 % RAFT-$(Man)_1$ modified substrate using a three-phase model (substrate/RAFT

layer/ambient air). Using fixed values n = 1.45 and k = 0.01, the thickness of the RAFT layer could be obtained: d = 2.26 ± 0.16 (mse = 2.66)

Table ESI-1. Summary of optical properties and thickness of various RAFT-Man modified gold substrates obtained by fitting Δ and ψ data (for incidence angle varying from 50° to 80°, by 2° step). The optical properties of substrate (n_s, k_s) were fitted using a two-phase model (substrate/ambient air). These values were used to fit the data of RAFT modified substrate using a three-phase model (substrate/RAFT layer/ambient air). The thickness (d) of the RAFT –layer was obtained assuming fixed values n = 1.45 and k = 0.01

	RAFT-Man modified substrate									
	100%		33%		20%		10%		5%	
	$(Man)_1$	$(Man)_4$	$(Man)_1$	$(Man)_4$	$(Man)_1$	$(Man)_4$	$(Man)_1$	$(Man)_4$	$(Man)_1$	$(Man)_4$
ns (± 0.011)	0.196	0.188	0.216	0.196	0.201	0.206	0.200	0.189	0.213	0.185
ks (± 0.011)	3.603	3.548	3.509	3.568	3.611	3.625	3.625	3.599	3.581	3.583
d (nm)	1.84	1.96	1.87	1.91	2.26	2.71	2.87	1.97	1.92	2.16

Con A interactions with RAFT-(Man)$_1$ and RAFT-(Man)$_4$ surfaces studied by QCM-D

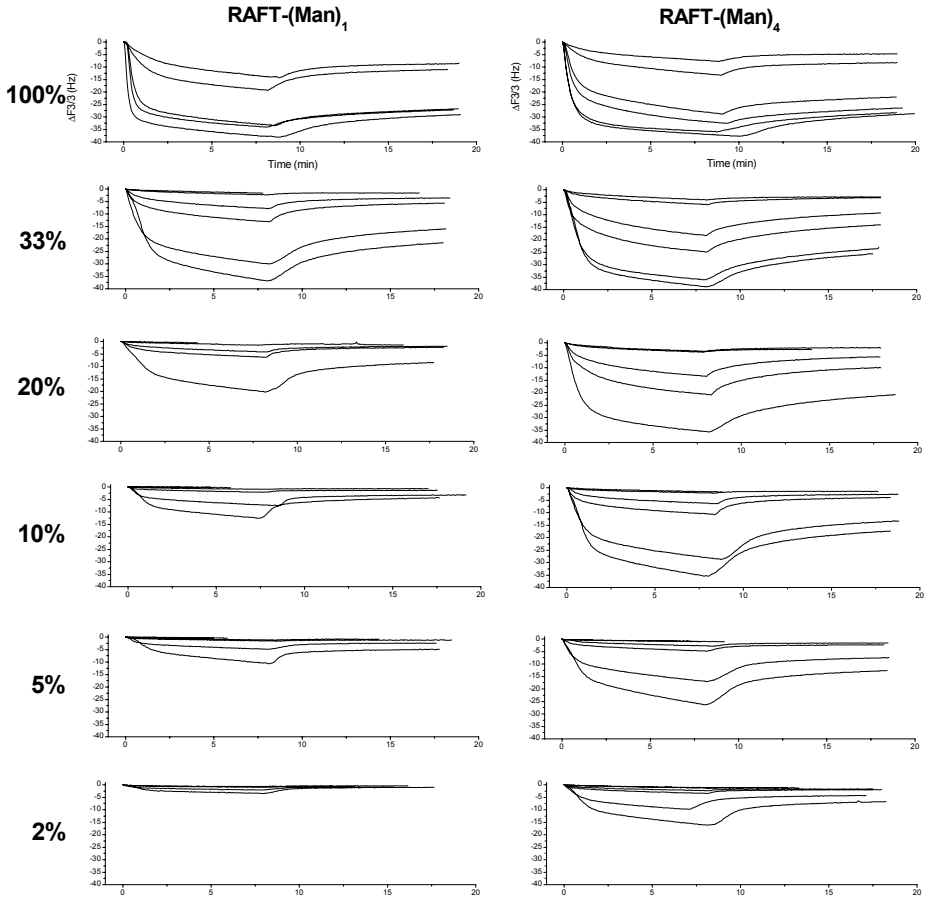

Fig. ESI-3. QCM-D response obtained for adsorption/desorption of Con A (from 0.049 µM to 9.8 µM, performed on RAFT-(Man)$_1$ and RAFT-(Man)$_4$ surfaces obtained by adsorption of solutions at six various RAFT-Mannose dilutions from 2% to 100 %. For clarity, only the frequency shift $\Delta f_n/n$ recorded for the third overtone is presented. Surface regeneration is performed by successive injections of 25 mM mannose solution and SDS 0.05 %. The experiments were performed in flow mode at 100 µL.min^{-1}.

Analysis of Con A binding using the rectangular hyperbolic relationship.

Quantification of multivalent interactions has been performed by applying the method reported by Winzor and co-workers [1, 2] for determining the affinity constant and the concentration of binding sites on the surface for multivalent interactions. This tool is based on the modified rectangular hyperbolic relationship (1):

$$Y = \frac{K_{AX}C_x^* \times X}{1 + K_{AX} \times X} \qquad (1)$$

where $Y = 2C_A^{*1/2}(C_A^{*1/2}\ C_A^{1/2})$ represents the Con A effective bound concentration and $X = 2C_A^{*1/2}\ C_A^{1/2}$ represents the effective injected concentration of Con A. From the raw SPR data at equilibrium, a plot of Y versus X can be generated (fig. ESI 3) from which the intrinsic dissociation constant K_{DX} and the effective concentration of binding sites C_x can be extracted.

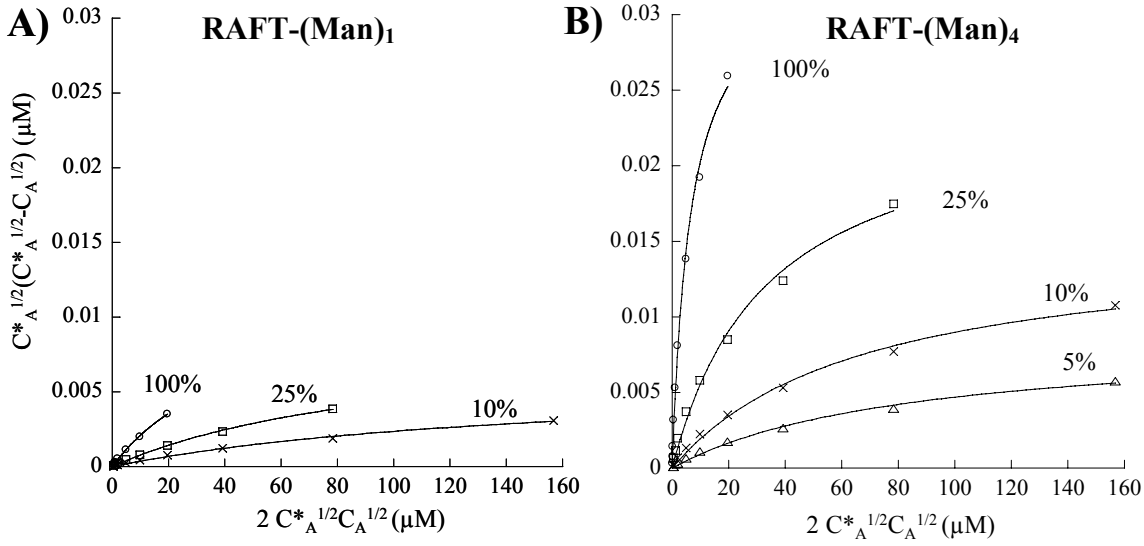

Fig. ESI-4. Plot of the effective concentration of Con A as a function of the effective injected concentration of ConA, as calculated from the raw SPR data obtained at equilibrium for the interaction of Con A with (A) RAFT-$(Man)_1$ and (B) RAFT-$(Man)_4$ surfaces at various RAFT-Mannose surface densities. The curves represent the best fits obtained from the modified rectangular hyperbolic relationship (1), by assuming a bivalent interaction of Con A with the surface (f = 2).

1 S. J. Harris, C. M. Jackson and D. J. Winzor, *Arch. Biochem. Biophys.*, 1995, **316**, 20-23.

2 N. L. Kalinin, L. D. Ward and D. J. Winzor, *Anal. Biochem.*, 1995, **228**, 238-244.