Supporting Information

Photogenerated Carbohydrate Microarrays to Study Carbohydrate-Protein Interactions using Surface Plasmon Resonance Imaging

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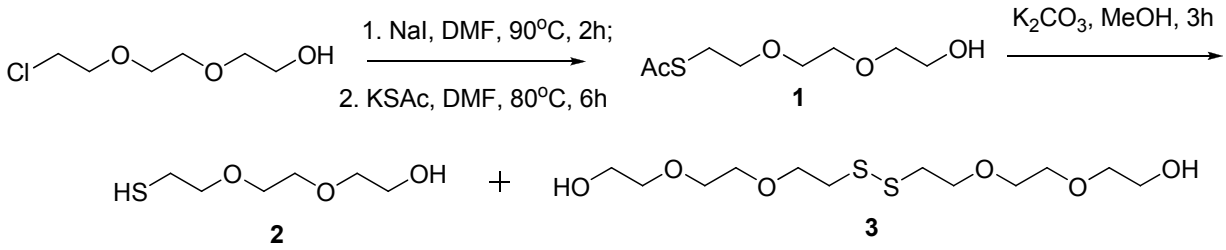
1. Synthesis of MDEG



***S*-2-(2-(2-Hydroxyethoxy)ethoxy)ethyl ethanethioate (1):** A solution of 2-(2-(2-chloroethoxy)ethoxy)ethanol (169 mg, 1 mmol) and sodium iodide (300 mg, 2 mmol) in DMF (4 mL) was stirred under nitrogen at 90 ˚C for 2 hours. After completion of the reaction detected by TLC, the solution was cooled to room temperature and potassium thioacetate (228 mg, 2 mmol) in DMF (2 mL) was added. The reaction was continued for another 6 hours at 80 ˚C. The solvent was then removed and the residue taken up in EtOAc/H_2O. The thiolate **1** was extracted with EtOAc and the organic phase collected and dried over Na_2SO_4. After evaporation of the solvent, the resulting residue was purified by flash column chromatography (SiO_2, hexane/EtOAc 1/4) to afford the thioate **1** in 71% yield. Characterization was in agreement with the literature (Kuijpers 1993).

2-(2-(2-Mercaptoethoxy)ethoxy)ethanol (2) and 3,6,13,16-tetraoxa-9,10-dithiaoctadecane-1,18-diol (3). Compound **1** (109 mg, 0.52 mmol) and potassium carbonate (287 mg, 2.08 mmol) were stirred in MeOH (4 mL) under nitrogen at room temperature for 3 hours. The solvent was then removed and the residue was purified by flash column chromatography (SiO_2, eluent 10/1 EtOAc/EtOH) to afford **2** and **3**, respectively, in a combined quantitative yield. Characterization was in agreement with the literature (Raehm 2002).

2. Typical SPRi image of printed array

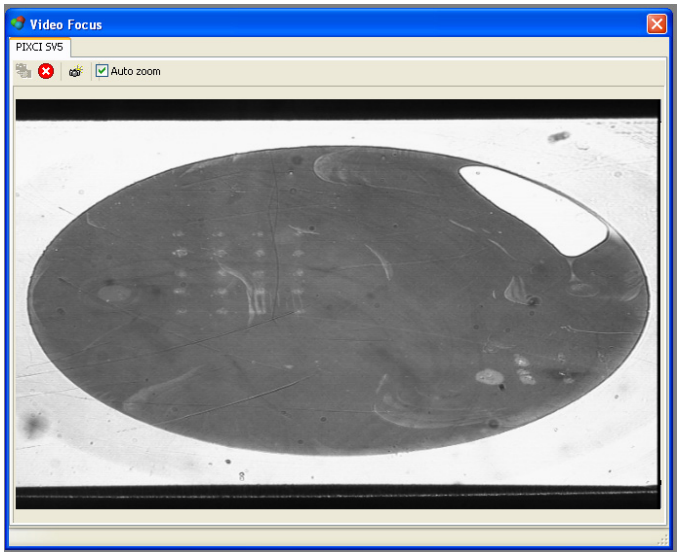
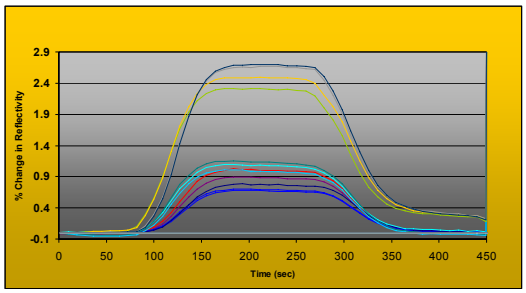


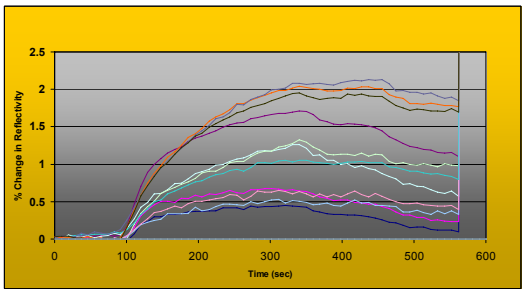
Figure 1S. SPRi image of printed array in PBS buffer. The carbohydrate microarray contained Man3, Man2, Man, Glc, and Gal, printed in quadruplets, fabricated on 90:10 mixed SAM of PFPA-MUTEG/MDEG.

3. Sensorgrams of Figure 1a

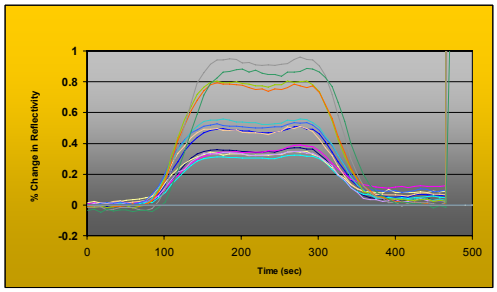
PFPA-MUTEG



PFPA-C_{11}-SH



PFPA-C_6-SH



PFPA-C_2-SH

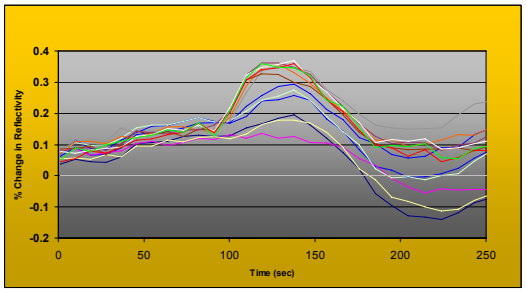
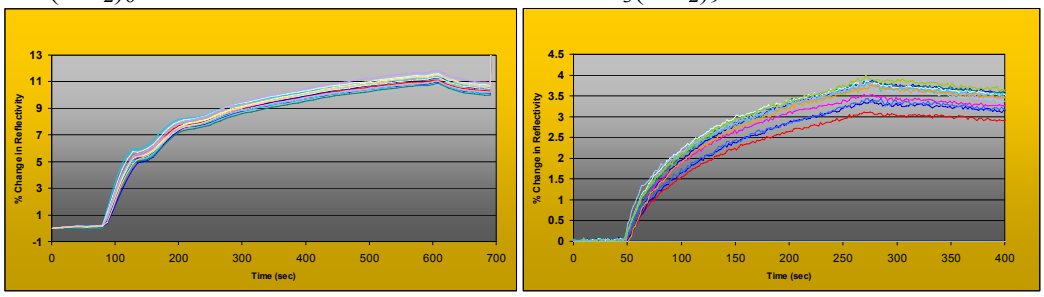


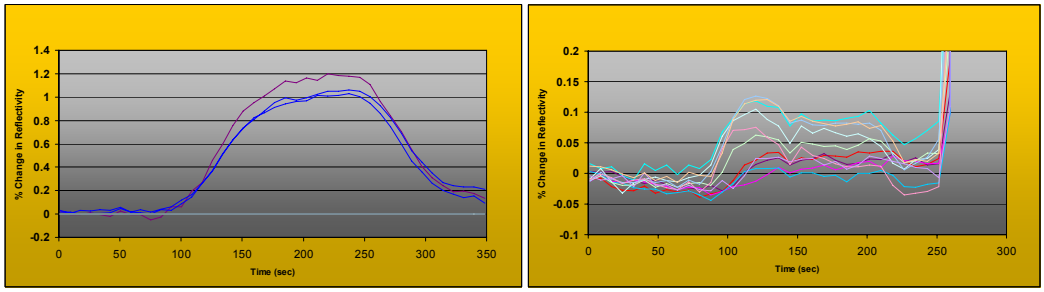
Figure 2S. Sensorgrams of Con A interacting with carbohydrate array fabricated on various PFPA surfaces. Man, Glc, and Gal were printed on the PFPA-functionalized SPR sensors in quadruplets, and the sensorgram of each printed spot was recorded simultaneously.

4. Sensorgrams of Figure 1b

$HO(CH_2)_6SH$ $CH_3(CH_2)_9SH$



MUTEG MDEG



Bare Au

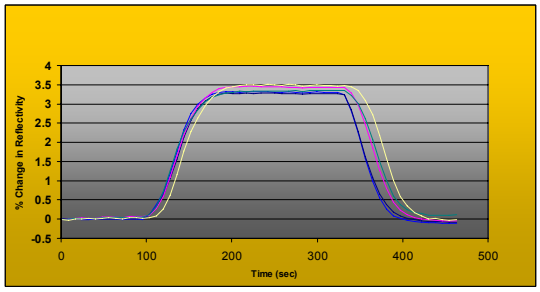


Figure 3S. Sensorgrams of Con A interacting with various surfaces. 5-12 spots were randomly chosen on the surface and the sensorgram of each spot was recorded simultaneously. The results shown in Figure 1b were the average of the responses for each surface.

5. Regeneration of microarray surface

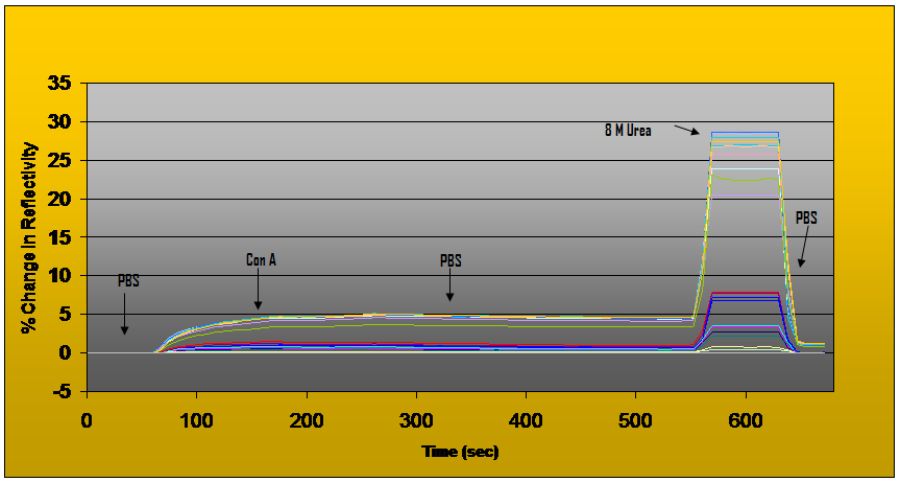


Figure 4S. SPR responses of carbohydrate microarrays containing Man3, Man2, Man, Glc, and Gal fabricated on 90:10 mixed SAM of PFPA-MUTEG/MDEG. Con A concentration was 10 nM.

6. Initial slopes of calibration curves

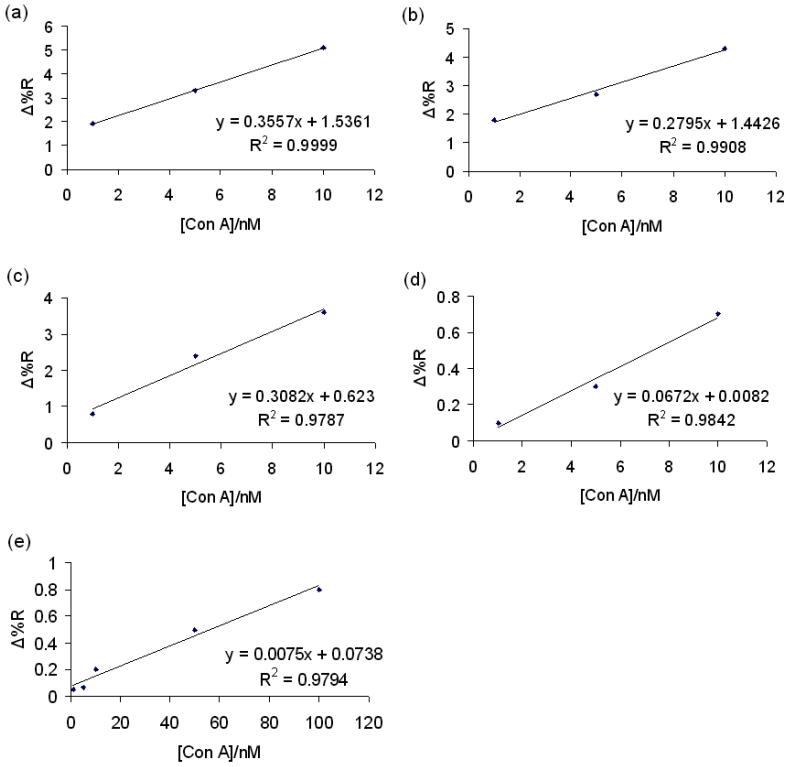


Figure 5S. Initial slopes of calibration curves for (a) Man3, (b) Man2, (c) Man, (d) Glc, and (e) Gal.

7. Contact angle analyses

Table 1S. θ_A, θ_R, and contact angle hysteresis of thiol-treated surfaces.

SAM	θ_A (°)[a]	θ_R (°)[a]	Hysteresis (°)
90:10 PFPA-MUTEG/MDEG	55.0±3.2	16.0±2.9	39.0
PFPA-MUTEG	79.0±2.0	15.1±2.6	63.9
PFPA-C_{11}-SH	102.7±1.9	90.6±2.5	12.1
$C_{12}H_{25}SH$	104.2±2.1	91.4±4.1	12.8
$C_{10}H_{21}SH$	101.3±3.3	79.3±3.2	22.0

[a]Results were the averages of three samples and measurements were made on three different spots on each sample.

8. Advancing and receding contact angles for SAMs

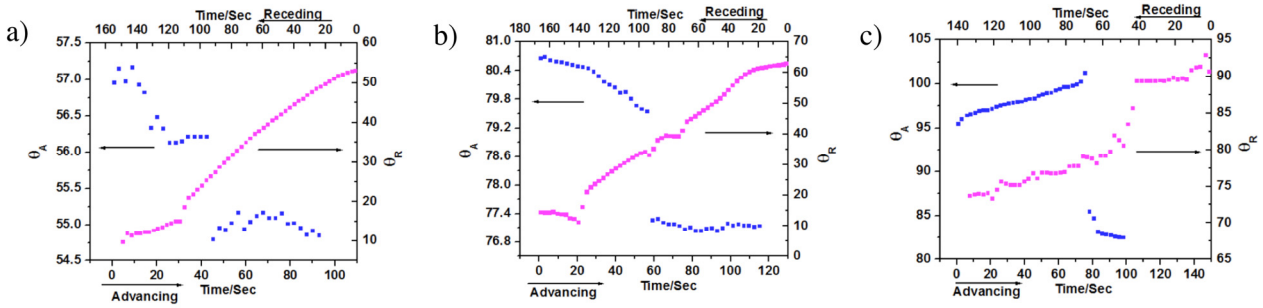


Figure 6S. Advancing and receding contact angles for SAMs formed from a) 90:10 PFPA-MUTEG/MDEG, b) PFPA-MUTEG, and c) PFPA-C_{11}-SH.

9. SPR responses with GS-II and SBA

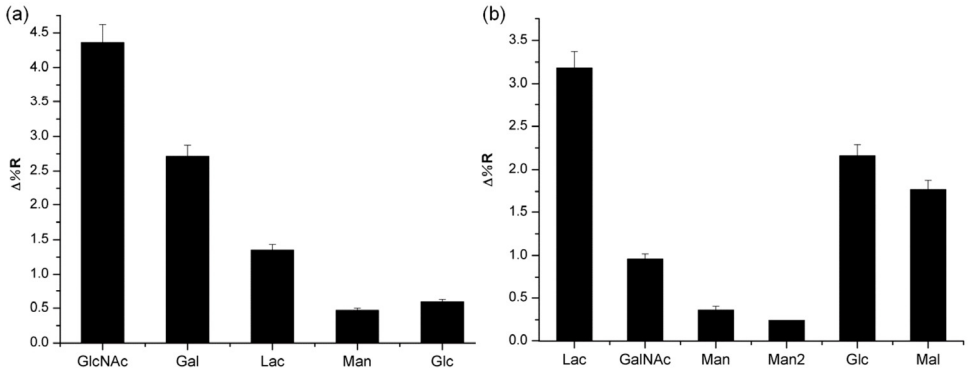


Figure 7S. SPR responses of arrayed carbohydrate ligands with a) GS-II, and b) SBA. Each data point was the average of three SPR sensors with four replicates for each ligand, and the error bar, therefore, represents the standard derivation of the 12 data points.

References

Kuijipers, W.H.A., Van Boeckel, C. A. A., **1993**. *Tetrahedron* 49, 10931-10944.

Raehm, L., Kern, J.-M., Sauvage, J.-P., Hamann, C., Palacin, S., Bourgoin, J.-P., **2002**. *Chem. Eur. J*. 8, 2153-2162.