Supporting Information

Direct discrimination of cell surface glycosylation signatures using a single pH-responsive boronic acid-functionalized polymer

Mingdi Jiang‡, Aritra Nath Chattopadhyay‡, Cheng Hsuan Li, Yingying Geng, David C. Luther, Rui Huang and Vincent M. Rotello*

Department of Chemistry, University of Massachusetts Amherst, 710 North Pleasant Street, Amherst, Massachusetts 01003, United States

*Corresponding author: rotello@chem.umass.edu

‡M. Jiang and A. N. Chattopadhyay contributed equally to the work.

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1. Synthesis of PONI-boronic acid (BA)-pyrene (PONI-BA-Pyrene)

The PONI-BA-Pyrene polymer was synthesized according to the following protocols.

![Synthesis reaction](image)

Synthesis of 1

24.5 g of dicyclopentadiene was melted in hot water (185 mmol, 1.0 eq) at 50°C for 10 minutes. 30 g of maleic anhydride (370 mmol, 2.0 eq) was brought to reflux in 60 mL of o-dichlorobenzene in a 250 mL round bottom flask. The liquid dicyclopentadiene was then transferred to the reaction flask dropwise over a time of 15 minutes. The reaction was left to run at reflux for another 1.5 hours. After that, the reaction was taken off the heat and allowed to cool down to room temperature. After 2 hours, the flask was transferred to the refrigerator to be kept overnight for cooling down. 12 hours later, the resulting crystalline solid was filtered off in vacuo. Multiple recrystallizations in boiling monochlorobenzene resulted in the isolation of the desired compound 1 with a high exo purity in a yield of 45%. 

$^1$H NMR (400 MHz, CDCl$_3$) 6.34 (s, 2H), 3.45 (s, 2H), 3.01 (s, 2H), 1.79 (d, J=11Hz, 2H), 1.57 (d, J=11Hz, 2H), p.p.m.

Synthesis of 2

To a 250 mL round bottom flask equipped with a stir bar was added 50 mL of toluene. Next, 1 (1 g, 6.09 mmol, 1.0 eq) was added along with 4-aminobutyric acid (0.69 g, 6.70 mmol, 1.1 eq). The reaction mixture was connected to a Dean-Stark trap and heated to 110 °C and it was left to run overnight. Afterwards, the reaction mixture was cooled down to room temperature, washed with 1M HCl (3x, 30 mL), water (3x, 30 mL) and brine (1x, 30 mL). The organic layer was dried with sodium sulfate, filtered and rotavaped. Column chromatography was performed to yield 2 as a white solid (76% yield). 

$^1$H NMR (400 MHz, CDCl$_3$) 6.32 (s, 2H), 3.55 (t, 2H), 3.28 (s, 2H), 2.70 (s, 2H), 2.39 (t, 2H), 1.92 (q, 2H), 1.53 (m, 1H), 1.21 (m, 1H).
Synthesis of 3

2 (1.1 g, 4.4 mmol, 1.1 eq), 4-hydroxyphenylboronic acid pinacol ester (0.9 g, 4.0 mmol, 1.0 eq) and 4-dimethylaminopyridine was mixed with dry THF and refluxed in a 250 ml round bottom flask. The mixture was stirred until everything got dissolved. After the solution was clear, pivalic anhydride (0.8 g, 4.4 mmol, 1.1 eq) was added to the reaction mixture. The reaction was kept stirring for 24 hours at reflux condition. After 24 hours, 5 ml of water was added to the reaction and stirred for 2 hours. Dichloromethane was added to the reaction mixture, washed with saturated sodium bicarbonate (3x) and brine (1x) and dried over MgSO₄. The mixture was filtered and concentrated on a rotary evaporator. Column chromatography was done in silica with 33% ethyl acetate in hexanes which resulted in a white solid (68% yield). ¹H NMR (400 MHz, CDCl₃) 7.82 (d, 2H), 7.10 (d, 2H), 6.27 (s, 2H), 3.61 (t, 2H), 3.28 (s, 2H), 2.69 (s, 2H), 2.58 (t, 2H), 2.00 (m, 2H), 1.55 (m, 2H), 1.33 (s, 12H).

Synthesis of 4

Pyrene butyric acid (2.0 g, 4.4 mmol, 1.1 eq) and N-hydroxysuccinimide (0.9 g, 4.0 mmol, 1.0 eq) were mixed and dissolved in dioxane in an ice bath. Dicyclohexycarbodiimide was added to the mixture at 0 °C and the reaction mixture was stirred for 15 mins. 4-dimethylaminopyridine was next added to the mixture at 0 °C and stirred for 1 hr in the ice bath. After 1 hr, the ice bath was removed, and the reaction was left to run overnight. After 18 hrs, the reaction was stopped, and the mixture was concentrated on a rotary evaporator. Column chromatography in silica with 50% ethyl acetate in hexanes yielded 4 as a yellowish white solid (37% yield). ¹H NMR (400 MHz, CDCl₃) 8.30 (d, 1H), 8.15 (m, 4H), 8.00 (m, 3H), 7.88 (d, 1H), 3.45 (t, 2H), 2.90 (s, 4H), 2.84 (t, 2H), 2.30 (p, 2H).
Synthesis of 6

Monomer 5 was synthesized following previous reports.\(^\text{1}\) 5 (0.60 g, 1.78 mmol, 1.0 eq) was added to a 250 ml round bottom flask equipped with a stir bar under N\(_2\) atmosphere at room temperature. Diisopropylethylamine (0.69 g, 5.35 mmol, 3.0 eq) and dichloromethane was added to the flask under N\(_2\) purging and the mixture was stirred. 4 (0.69 g, 1.78 mmol, 1.0 eq) was slowly added to the reaction and the mixture was stirred for 4 hr at room temperature. Column chromatography was done in silica in pure ethyl acetate to get the product as a slight yellow solid (63% yield). \(^\text{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.34 (d, 1H), 8.18 (m, 4H), 8.00 (m, 3H), 7.88 (d, 1H), 6.48 (s, 2H), 6.17 (s, 1H), 5.21 (s, 2H), 3.54 (t, 2H), 3.42 (t, 2H), 3.18 (m, 2H), 2.39 (t, 2H), 2.25 (m, 2H), 1.76 (m, 2H), 1.60 (s, 1H).

Polymer synthesis scheme:

Monomer 7 was also synthesized following previous reports.\(^\text{1}\) To a 15 mL pear-shaped air-free flask equipped with a stir bar was added 3 (50 mg, 0.10 mmol, 2.0 eq), 7 (126 mg, 0.33 mmol, 7.0 eq), 6 (25 mg, 0.05 mmol, 1.0 eq) and 5 mL of DCM. In a separate 10 ml pear-shaped air-free flask was added Grubbs’ 3\(^{\text{rd}}\) generation catalyst (10.0 mg, 0.012 mmol) and 1 mL DCM. Both flasks were sealed with septa and attached to a Schlenk nitrogen/vacuum line. Both flasks were freeze-pump-thawed three times. After thawing, Grubbs’ 3\(^{\text{rd}}\) generation catalyst was removed via syringe and quickly added to the flask containing 3, 7 & 6 and allowed to react for 90 mins. After the allotted time, ethyl vinyl ether (300 \(\mu\)L) was added and allowed to stir for 20 mins. Afterwards, the reaction was diluted to two times the volume and precipitated into a heavily stirred solution of a 1:1 mixture of ethyl ether and hexane. The precipitated polymer
was filtered and dissolved into tetrahydrofuran (THF). The polymer was precipitated again into the same mixture solvent and filtered. After filtration, the residue was dissolved in 5 mL of DCM and 5 mL of trifluoroacetic acid was added to the mixture. Then (160 mg, 5.0 eq) of methylboronic acid was added to the mixture and the reaction was allowed to run overnight. Afterwards, the solvent was completely evaporated and washed with hexane 2 times and dissolved into a minimal amount of water. The polymers were added to 10,000 MWCO dialysis membranes and allowed to stir for 3 days in Milli Q water, changing the water periodically. The polymers were filtered through PES syringe filters and freeze-dried to yield **PONI-BA-Py**.

1H NMR (400MHz, CDCl$_3$) 8.37 (m, 2H), 8.23 (m, 6H), 8.11 (s, 4H), 8.02 (s, 3H), 7.93 (m, 2H), 7.81 (d, 6H), 7.7 (s, 1H), 7.05 (s, 6H), 5.93 (s, 12H), 5.70 (s, 19H), 4.84 (s, 12H), 4.37 (s, 12H), 3.45 (d, 280H), 3.20 (s, 38H), 3.07 (s, 11H), 2.54 (m, 6H), 2.22 (s, 3H), 2.00 (s, 4H), 1.83 (s, 5H), 1.63 (s, 3H), 1.28 (s, 7H). The polymer was also characterized by GPC (gel permeation chromatography) in tetrahydrofuran. The MW was ~30,000 and the PDI (polydispersity index) was 1.01.

2. Characterization of the PONI-BA-Pyrene polymer sensor

2.1 Gel permeation chromatography (GPC)

![Figure S1](image1.png)

**Figure S1.** Characterization of Boc-protected polymer using gel permeation chromatography. GPC trace shows that the **PONI-BA-pyrene** has Mw = 30 kDa and Mn = 29.5 kDa and a polydispersity index of 1.01, determined by GPC using polystyrene standards, THF as solvent and toluene as the flow marker.

2.2 Transmission Electron Microscopy (TEM) of PONI-BA-pyrene

![Image2.png]
2.3 Dynamic light scattering (DLS) of PONI-BA-pyrene

Figure S2. TEM image of PONI-BA-pyrene used in the study, which was taken under 30,000× magnification.

2.4 Fluorescence response of PONI-BA-pyrene under different pH

Figure S3. Hydrodynamic sizes of PONI-BA-pyrene polymers in 5 mM phosphate buffers with different pH values. The sizes of PONI-BA-pyrene under pH 5.8, 7.4, and 8.2 are approximately 14.0 ±5.0, 19.4 ±4.7, and 15.6 ±2.7 nm, respectively, which indicates the size of polymer is stable upon changing pH values.

3. Interaction between boronic acid and diol

3.1 Fluorescence response of PONI-BA-pyrene incubating with different concentrations of saccharides

Figure S4. Fluorescence intensities of 40 µg/L PONI-BA-pyrene under different pH, with the monomer emission of 398 nm and excimer emission of 473 nm at the excitation of 330 nm. Each value is the average of eight parallel measurements (n=8).
Figure S5. Variation of fluorescence intensity with the increase in concentration of saccharides. a) Galactose. b) Lactose. c) Sucrose.

3.2 FT-IR studies with norborneneimide-based boronic acid monomer

Synthesis of norborneneimide-based boronic acid monomer (NI-BA):

3 (250 mg, 0.55 mmol, eq) was taken in a 20 mL vial, and a 5 mL 1:1 mixture of TFA and DCM was added to it and stirred. Then (166 mg, 2.77 mmol, 5.0 eq) of methylboronic acid was added to the mixture and the reaction was allowed to run overnight. Afterwards, the solvent was completely evaporated and dried under vacuum to remove the methylboronic acid to yield NI-BA or 8. 1H NMR (400 MHz, CDCl₃) 7.75 (d, 2H), 7.11 (d, 2H), 6.32 (t, 2H), 4.81 (s, 5H), 3.59 (t, 2H), 3.30 (t, 2H), 3.20 (s, 2H), 2.73 (s, 2H), 2.61 (t, 2H), 1.96 (m, 2H).

Figure S6. FT-IR spectra of NI-BA
Figure S7. FTIR data for binding studies of NI-BA when interacting with saccharides. The difference spectra of NI-BA in the presence of a) 4 mg/mL of galactose and b) 4 mg/mL of mannose pentaacetate as control in the region of O-H stretching frequency to NI-BA only. The difference spectra of NI-BA in the presence of c) 4 mg/mL of galactose and d) 4 mg/mL mannose pentaacetate as control in the region of B-O and C-O stretching frequency.

3.3 pH-responsiveness of binding between boronic acid and diol

Scheme S1. The interaction between boronic acids and cis-diol-containing substances under different pH environment.
4. Sensing data

4.1 Sensing data for discrimination of cancer cell types

Table S1. Normalized fluorescence responses and LDA output for non-tumorigenic or tumorigenic cells. Score (1) and score (2) correspond to Figure 3 in the main text.

| Sample name | pH 5.8-Monomer | pH 5.8-Excimer | pH 7.4-Monomer | pH 7.4-Excimer | pH 8.2-Monomer | pH 8.2-Excimer | LDA output |
|-------------|----------------|---------------|----------------|---------------|----------------|---------------|------------|
|             | $I_n/I_0$       |               | $I_n/I_0$       |               | $I_n/I_0$       |               |            |
| MCF10A      | 1.021           | 1.060         | 0.990          | 0.990         | 1.036          | 1.036         | 1.667      |
| MCF10A      | 1.023           | 1.045         | 1.030          | 1.044         | 1.053          | 1.018         | 2.702      |
| MCF10A      | 1.060           | 1.118         | 0.997          | 0.995         | 1.050          | 1.067         | 1.388      |
| MCF10A      | 1.054           | 1.094         | 1.018          | 1.057         | 1.066          | 1.049         | 3.069      |
| MCF10A      | 1.054           | 1.090         | 1.042          | 1.058         | 1.077          | 1.075         | 2.337      |
| MCF-7       | 1.087           | 1.145         | 1.077          | 1.108         | 1.081          | 1.065         | 1.235      |
| MCF-7       | 1.057           | 1.120         | 1.092          | 1.203         | 1.055          | 1.024         | -1.028     |
| MCF-7       | 1.042           | 1.064         | 1.082          | 1.173         | 1.029          | 0.991         | 0.139      |
| MCF-7       | 1.044           | 1.091         | 1.065          | 1.153         | 1.014          | 0.950         | -0.23      |
| MCF-7       | 1.061           | 1.096         | 1.079          | 1.153         | 1.008          | 0.963         | -0.628     |
| MCF-7       | 1.067           | 1.106         | 1.076          | 1.139         | 1.024          | 0.949         | 0.983      |
| MCF-7       | 1.099           | 1.152         | 1.091          | 1.167         | 1.044          | 1.001         | 0.385      |
| HeLa        | 1.015           | 1.031         | 1.078          | 1.136         | 1.135          | 1.098         | 4.666      |
| HeLa        | 1.037           | 1.061         | 1.038          | 1.050         | 1.109          | 1.079         | 4.946      |
| HeLa        | 1.007           | 1.012         | 1.049          | 1.051         | 1.098          | 1.037         | 5.294      |
| HeLa        | 1.033           | 1.064         | 1.051          | 1.056         | 1.093          | 0.994         | 5.404      |
| HeLa        | 1.024           | 1.046         | 1.063          | 1.069         | 1.120          | 1.043         | 5.779      |
| HeLa        | 1.043           | 1.076         | 1.078          | 1.096         | 1.159          | 1.121         | 5.547      |
| 3T3         | 1.095           | 1.231         | 1.125          | 1.001         | 1.094          | 1.315         | -10.933    |
| 3T3         | 1.090           | 1.227         | 1.143          | 1.099         | 1.129          | 1.334         | -9.695     |
| 3T3         | 1.117           | 1.259         | 1.116          | 1.030         | 1.068          | 1.262         | -10.702    |
| 3T3         | 1.106           | 1.247         | 1.111          | 1.055         | 1.141          | 1.363         | -8.297     |
| 3T3         | 1.077           | 1.210         | 1.139          | 1.098         | 1.094          | 1.156         | -6.895     |
| 3T3         | 1.074           | 1.209         | 1.207          | 1.035         | 1.122          | 1.249         | -10.503    |
| 4T1         | 1.055           | 1.142         | 0.997          | 1.006         | 1.187          | 1.298         | 3.033      |
| 4T1         | 1.079           | 1.197         | 1.014          | 1.017         | 1.149          | 1.180         | 2.09       |
| 4T1         | 1.121           | 1.245         | 0.984          | 0.979         | 1.174          | 1.265         | 3.163      |
| 4T1         | 1.113           | 1.208         | 1.024          | 1.023         | 1.152          | 1.208         | 2.999      |
| 4T1         | 1.110           | 1.268         | 1.042          | 1.060         | 1.188          | 1.255         | 0.32       |
| 4T1         | 1.136           | 1.239         | 1.064          | 1.098         | 1.176          | 1.260         | 1.756      |

Table S2. Percentage of accurate classification of cell types from Jackknifed analysis. The results show an overall 100% correct classification.
Table S3. Prediction of unknown cell types using training set from Figure 3 and Table S1. The results show an overall 93% correct unknown identification.

| Unknown sample # | pH 5.8-Monomer | pH 5.8-Excimer | pH 7.4-Monomer | pH 7.4-Excimer | pH 8.2-Monomer | pH 8.2-Excimer | True ID | Identified as | Correct prediction |
|------------------|----------------|----------------|----------------|----------------|----------------|----------------|---------|--------------|-------------------|
| 1                | 1.022          | 1.034          | 1.003          | 0.999          | 0.999          | 1.034          | MCF10A  | MCF10A       | Yes               |
| 2                | 1.013          | 1.059          | 1.001          | 0.988          | 0.997          | 0.953          | MCF10A  | MCF10A       | Yes               |
| 3                | 1.000          | 0.984          | 0.980          | 0.978          | 1.028          | 0.995          | MCF10A  | MCF10A       | Yes               |
| 4                | 1.008          | 1.006          | 1.005          | 1.010          | 1.033          | 1.007          | MCF10A  | MCF10A       | Yes               |
| 5                | 1.053          | 1.076          | 0.957          | 0.961          | 1.042          | 1.019          | MCF10A  | MCF10A       | Yes               |
| 6                | 1.052          | 1.097          | 0.970          | 0.991          | 1.075          | 1.050          | MCF10A  | MCF10A       | Yes               |
| 7                | 1.054          | 1.135          | 1.058          | 1.136          | 1.146          | 1.139          | MCF7    | HeLa         | No                |
| 8                | 1.053          | 1.125          | 1.059          | 1.143          | 1.065          | 1.026          | MCF7    | MCF7         | Yes               |
| 9                | 1.066          | 1.148          | 1.073          | 1.131          | 1.048          | 1.011          | MCF7    | MCF7         | Yes               |
| 10               | 1.080          | 1.215          | 1.086          | 1.154          | 1.035          | 0.991          | MCF7    | MCF7         | Yes               |
| 11               | 1.092          | 1.190          | 1.100          | 1.187          | 1.044          | 1.009          | MCF7    | MCF7         | Yes               |
| 12               | 1.086          | 1.174          | 1.122          | 1.222          | 1.033          | 0.986          | MCF7    | MCF7         | Yes               |
| 13               | 1.024          | 1.045          | 1.047          | 1.037          | 1.125          | 1.108          | HeLa    | HeLa         | Yes               |
| 14               | 1.043          | 1.065          | 1.031          | 1.023          | 1.118          | 1.110          | HeLa    | HeLa         | Yes               |
| 15               | 1.046          | 1.074          | 1.091          | 1.096          | 1.221          | 1.190          | HeLa    | HeLa         | Yes               |
| 16               | 1.032          | 1.063          | 1.057          | 1.048          | 1.058          | 1.061          | MCF10A  | MCF10A       | No                |
| 17               | 1.066          | 1.102          | 1.046          | 1.020          | 1.167          | 1.170          | HeLa    | HeLa         | Yes               |
| 18               | 1.056          | 1.127          | 1.095          | 1.096          | 1.171          | 1.005          | HeLa    | HeLa         | Yes               |
| 19               | 1.094          | 1.252          | 1.157          | 1.088          | 1.114          | 1.363          | 3T3     | 3T3          | Yes               |
| 20               | 1.094          | 1.243          | 1.155          | 1.098          | 1.077          | 1.270          | 3T3     | 3T3          | Yes               |
| 21               | 1.062          | 1.158          | 1.151          | 1.052          | 1.110          | 1.308          | 3T3     | 3T3          | Yes               |
| 22               | 1.057          | 1.178          | 1.159          | 1.028          | 1.074          | 1.283          | 3T3     | 3T3          | Yes               |
| 23               | 1.077          | 1.222          | 1.192          | 1.091          | 1.106          | 1.309          | 3T3     | 3T3          | Yes               |
| 24               | 1.082          | 1.236          | 1.155          | 1.028          | 1.083          | 1.168          | 3T3     | 3T3          | Yes               |
| 25               | 1.037          | 1.113          | 1.016          | 1.002          | 1.120          | 1.204          | 4T1     | 4T1          | Yes               |
| 26               | 1.043          | 1.118          | 1.005          | 0.967          | 1.141          | 1.198          | 4T1     | 4T1          | Yes               |
| 27               | 1.030          | 1.084          | 0.994          | 0.966          | 1.129          | 1.190          | 4T1     | 4T1          | Yes               |
| 28               | 1.025          | 1.112          | 1.013          | 0.992          | 1.130          | 1.211          | 4T1     | 4T1          | Yes               |
| 29               | 1.067          | 1.186          | 1.012          | 1.024          | 1.150          | 1.251          | 4T1     | 4T1          | Yes               |
| 30               | 1.083          | 1.231          | 1.038          | 1.057          | 1.173          | 1.235          | 4T1     | 4T1          | Yes               |
4.2 Sensing data for identification of Chinese hamster ovary (CHO) mutated cells.

Table S4. Normalized fluorescence responses and LDA output for CHO cell lines. Score (1) and score (2) correspond to Figure 4 in the main text.

| Sample name | pH 5.8-Monomer | pH 5.8-Excimer | pH 7.4-Monomer | pH 7.4-Excimer | pH 8.2-Monomer | pH 8.2-Excimer | LDA output |
|-------------|----------------|----------------|----------------|----------------|----------------|----------------|------------|
|             | I_0/I_0        | Score (1)      | Score (2)      | Score (1)      | Score (2)      | Score (1)      | Score (2)  |
| CRL-2241    | 1.018          | 1.118          | 0.903          | 1.040          | 0.893          | 1.075          | -4.115     | -2.443     |
| CRL-2241    | 1.037          | 1.101          | 0.906          | 1.007          | 0.910          | 1.120          | -3.739     | -2.259     |
| CRL-2241    | 1.016          | 1.101          | 0.889          | 1.014          | 0.886          | 1.102          | -3.396     | -3.486     |
| CRL-2241    | 1.037          | 1.092          | 0.865          | 1.017          | 0.916          | 1.097          | -4.353     | -3.824     |
| CRL-2241    | 1.048          | 1.083          | 0.855          | 0.993          | 0.889          | 1.065          | -4.956     | -3.792     |
| CRL-2241    | 1.016          | 1.061          | 0.883          | 1.011          | 0.889          | 1.088          | -3.928     | -4.064     |
| CRL-1735    | 1.130          | 1.183          | 0.928          | 1.189          | 0.982          | 1.175          | 3.110      | -0.822     |
| CRL-1735    | 1.108          | 1.159          | 0.938          | 1.170          | 0.962          | 1.214          | 4.230      | -2.220     |
| CRL-1735    | 1.112          | 1.192          | 0.880          | 1.144          | 0.929          | 1.190          | 4.799      | -3.238     |
| CRL-1735    | 1.092          | 1.189          | 0.910          | 1.255          | 0.978          | 1.228          | 7.437      | -4.008     |
| CRL-1735    | 1.042          | 1.149          | 0.905          | 1.152          | 0.836          | 1.105          | 4.431      | -4.457     |
| CRL-1735    | 1.044          | 1.120          | 0.925          | 1.149          | 0.880          | 1.139          | 3.887      | -3.835     |
| CRL-1736    | 1.204          | 1.229          | 1.006          | 1.241          | 1.019          | 1.244          | 6.971      | 3.159      |
| CRL-1736    | 1.238          | 1.229          | 1.016          | 1.251          | 1.043          | 1.295          | 9.022      | 3.557      |
| CRL-1736    | 1.244          | 1.252          | 1.014          | 1.292          | 1.009          | 1.244          | 10.007     | 3.623      |
| CRL-1736    | 1.219          | 1.223          | 1.008          | 1.299          | 1.017          | 1.240          | 9.417      | 2.606      |
| CRL-1736    | 1.226          | 1.252          | 0.979          | 1.217          | 1.021          | 1.288          | 8.256      | 2.399      |
| CRL-1736    | 1.225          | 1.247          | 1.016          | 1.307          | 0.992          | 1.212          | 9.639      | 3.367      |
| CRL-2242    | 1.050          | 1.085          | 0.893          | 1.101          | 0.903          | 1.079          | -1.119     | -3.614     |
| CRL-2242    | 1.049          | 1.105          | 0.877          | 1.099          | 0.898          | 1.116          | 0.550      | -4.675     |
| CRL-2242    | 1.047          | 1.087          | 0.864          | 1.077          | 0.881          | 1.099          | 0.005      | -5.240     |
| CRL-2242    | 1.048          | 1.083          | 0.849          | 1.073          | 0.925          | 1.160          | 0.462      | -6.151     |
| CRL-2242    | 1.054          | 1.093          | 0.847          | 1.046          | 0.911          | 1.166          | 0.465      | -5.911     |
| CRL-2242    | 1.032          | 1.080          | 0.849          | 1.066          | 0.902          | 1.140          | 0.172      | -6.390     |
| CCL-61      | 1.069          | 1.107          | 0.972          | 1.029          | 0.949          | 1.011          | -9.415     | 3.332      |
| CCL-61      | 1.067          | 1.091          | 0.974          | 1.029          | 0.940          | 1.020          | -8.492     | 2.839      |
| CCL-61      | 1.128          | 1.101          | 0.960          | 1.014          | 0.937          | 0.993          | -8.807     | 3.990      |
| CCL-61      | 1.085          | 1.131          | 0.948          | 1.015          | 0.935          | 1.022          | -8.486     | 2.689      |
| CCL-61      | 1.073          | 1.087          | 0.927          | 1.005          | 0.926          | 0.990          | -9.594     | 1.452      |
| CCL-61      | 1.043          | 1.079          | 0.942          | 0.996          | 0.935          | 0.989          | -11.013    | 1.772      |
| CRL-2244    | 1.265          | 1.173          | 1.041          | 1.129          | 1.011          | 1.155          | 0.695      | 7.717      |
| CRL-2244    | 1.219          | 1.178          | 1.041          | 1.158          | 1.024          | 1.175          | 1.035      | 6.539      |
| CRL-2244    | 1.186          | 1.153          | 1.023          | 1.133          | 1.009          | 1.135          | -1.272     | 5.598      |
| CRL-2244    | 1.222          | 1.179          | 1.019          | 1.154          | 1.011          | 1.130          | -0.250     | 6.203      |
| CRL-2244    | 1.192          | 1.168          | 0.996          | 1.138          | 1.005          | 1.145          | 0.293      | 4.463      |
| CRL-2244    | 1.189          | 1.158          | 1.007          | 1.128          | 0.997          | 1.120          | -1.364     | 5.125      |
Table S5. Percentage of accurate classification of CHO glycosylation mutants from Jackknifed analysis. The results show an overall 100% correct classification.

| Unknown cell type | CCL-61 | CRL-1735 | CRL-1736 | CRL-2241 | CRL-2242 | CRL-2244 | Correct (%) |
|-------------------|--------|----------|----------|----------|----------|----------|-------------|
| CCL-61            | 6      | 0        | 0        | 0        | 0        | 0        | 100         |
| CRL-1735          | 0      | 6        | 0        | 0        | 0        | 0        | 100         |
| CRL-1736          | 0      | 0        | 6        | 0        | 0        | 0        | 100         |
| CRL-2241          | 0      | 0        | 0        | 6        | 0        | 0        | 100         |
| CRL-2242          | 0      | 0        | 0        | 0        | 6        | 0        | 100         |
| CRL-2244          | 0      | 0        | 0        | 0        | 6        | 0        | 100         |
| Total             | 6      | 6        | 6        | 6        | 6        | 6        | 100         |

Table S6. Prediction of unknown cell types using training set from Figure 4 and Table S4. The results show an overall 100% correct unknown identification.

| Unknown sample # | pH 5.8- Monomer | pH 5.8- Excimer | pH 7.4- Monomer | pH 7.4-Excimer | pH 8.2- Monomer | pH 8.2-Excimer | True ID | Identified as | Correct prediction |
|------------------|------------------|------------------|------------------|----------------|------------------|----------------|---------|---------------|---------------------|
| 1                | 1.033            | 1.101            | 0.803            | 1.028          | 0.865            | 1.015          | CRL-2241 | CRL-2241      | Yes                 |
| 2                | 1.022            | 1.110            | 0.821            | 1.039          | 0.882            | 1.072          | CRL-2241 | CRL-2241      | Yes                 |
| 3                | 1.026            | 1.100            | 0.808            | 1.030          | 0.858            | 1.029          | CRL-2241 | CRL-2241      | Yes                 |
| 4                | 1.013            | 1.099            | 0.847            | 1.021          | 0.870            | 1.015          | CRL-2241 | CRL-2241      | Yes                 |
| 5                | 1.046            | 1.097            | 0.810            | 0.992          | 0.866            | 1.044          | CRL-2241 | CRL-2241      | Yes                 |
| 6                | 1.014            | 1.080            | 0.825            | 1.009          | 0.865            | 1.035          | CRL-2241 | CRL-2241      | Yes                 |
| 7                | 1.022            | 1.156            | 0.980            | 1.122          | 0.952            | 1.150          | CRL-1735 | CRL-1735      | Yes                 |
| 8                | 1.120            | 1.172            | 0.986            | 1.185          | 0.986            | 1.188          | CRL-1735 | CRL-1735      | Yes                 |
| 9                | 1.109            | 1.176            | 0.975            | 1.144          | 0.982            | 1.221          | CRL-1735 | CRL-1735      | Yes                 |
| 10               | 1.111            | 1.178            | 0.972            | 1.146          | 0.977            | 1.196          | CRL-1735 | CRL-1735      | Yes                 |
| 11               | 1.094            | 1.149            | 0.964            | 1.139          | 0.948            | 1.157          | CRL-1735 | CRL-1735      | Yes                 |
| 12               | 1.093            | 1.144            | 0.946            | 1.102          | 0.956            | 1.153          | CRL-1735 | CRL-1735      | Yes                 |
| 13               | 1.237            | 1.260            | 1.022            | 1.185          | 1.023            | 1.226          | CRL-1736 | CRL-1736      | Yes                 |
| 14               | 1.182            | 1.225            | 1.052            | 1.258          | 1.025            | 1.229          | CRL-1736 | CRL-1736      | Yes                 |
| 15               | 1.221            | 1.238            | 1.028            | 1.204          | 0.974            | 1.239          | CRL-1736 | CRL-1736      | Yes                 |
| 16               | 1.171            | 1.202            | 1.038            | 1.230          | 1.017            | 1.209          | CRL-1736 | CRL-1736      | Yes                 |
| 17               | 1.227            | 1.213            | 1.009            | 1.192          | 1.024            | 1.229          | CRL-1736 | CRL-1736      | Yes                 |
| 18               | 1.180            | 1.201            | 1.008            | 1.164          | 0.991            | 1.194          | CRL-1736 | CRL-1736      | Yes                 |
| 19               | 1.051            | 1.085            | 0.919            | 1.094          | 0.902            | 1.061          | CRL-2242 | CRL-2242      | Yes                 |
| 20               | 1.061            | 1.101            | 0.916            | 1.112          | 0.936            | 1.125          | CRL-2242 | CRL-2242      | Yes                 |
| 21               | 1.059            | 1.084            | 0.927            | 1.106          | 0.831            | 1.065          | CRL-2242 | CRL-2242      | Yes                 |
| 22               | 1.062            | 1.083            | 0.911            | 1.119          | 0.920            | 1.133          | CRL-2242 | CRL-2242      | Yes                 |
| 23               | 1.070            | 1.085            | 0.901            | 1.099          | 0.907            | 1.105          | CRL-2242 | CRL-2242      | Yes                 |
| 24               | 1.032            | 1.053            | 0.910            | 1.068          | 0.905            | 1.114          | CRL-2242 | CRL-2242      | Yes                 |
| 25               | 1.084            | 1.125            | 0.934            | 1.019          | 0.968            | 1.047          | CCL-61   | CCL-61        | Yes                 |
| 26               | 1.084            | 1.105            | 0.914            | 1.015          | 0.936            | 1.034          | CCL-61   | CCL-61        | Yes                 |
|   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|
| 27 | 1.054 | 1.099 | 0.904 | 1.015 | 0.926 | 1.017 |   |   |
| 28 | 1.077 | 1.104 | 0.902 | 0.999 | 0.922 | 1.029 | CCL-61 | CCL-61 |
| 29 | 1.077 | 1.086 | 0.901 | 0.999 | 0.919 | 1.038 | CCL-61 | CCL-61 |
| 30 | 1.046 | 1.101 | 0.917 | 1.015 | 0.917 | 1.024 | CCL-61 | CCL-61 |
| 31 | 1.193 | 1.184 | 0.996 | 1.125 | 1.007 | 1.170 | CRL-2244 | CRL-2244 |
| 32 | 1.208 | 1.184 | 0.967 | 1.149 | 1.015 | 1.209 | CRL-2244 | CRL-2244 |
| 33 | 1.222 | 1.197 | 0.985 | 1.139 | 1.009 | 1.190 | CRL-2244 | CRL-2244 |
| 34 | 1.198 | 1.189 | 0.997 | 1.164 | 1.007 | 1.205 | CRL-2244 | CRL-2244 |
| 35 | 1.213 | 1.201 | 0.978 | 1.128 | 0.984 | 1.141 | CRL-2244 | CRL-2244 |
| 36 | 1.193 | 1.191 | 0.996 | 1.125 | 0.991 | 1.174 | CRL-2244 | CRL-2244 |

[1] R. F. Landis, C. H. Li, A. Gupta, Y. W. Lee, M. Yazdani, N. Ngernyuang, I. Altinbasak, S. Mansoor, M. A. S. Khichi, A. Sanyal, V. M. Rotello, *J. Am. Chem. Soc.* 2018, 140, 6176–6182.