Supporting Information (SI) for

The complexity and dynamics of the tissue glycoproteome associated with prostate cancer progression

Rebeca Kawahara\textsuperscript{1,2,3}, Saulo Recuero\textsuperscript{4}, Miguel Srougi\textsuperscript{4}, Katia R.M. Leite\textsuperscript{4}, Morten Thaysen-Andersen\textsuperscript{2,3\#§}, and Giuseppe Palmisano\textsuperscript{1\#§}

\textsuperscript{1}Instituto de Ciências Biomédicas, Departamento de Parasitologia, Universidade de São Paulo, USP, São Paulo, Brazil.
\textsuperscript{2}Department of Molecular Sciences, Macquarie University, Sydney, NSW, Australia
\textsuperscript{3}Biomolecular Discovery Research Centre, Macquarie University, Sydney, NSW, Australia
\textsuperscript{4}Laboratório de Investigação Médica da Disciplina de Urologia da Faculdade de Medicina da USP, LIM55, São Paulo, Brazil.

\# These authors share authorship

* To whom correspondence should be addressed:

i. GlycoProteomics Laboratory, Department of Parasitology, Institute of Biomedical Sciences, University of São Paulo, Avenida Lineu Prestes 1374, CEP: 05508-000, São Paulo, Brazil. Email: palmisano.gp@usp.br

ii. Department of Molecular Sciences, Macquarie University, Sydney, NSW 2109, Australia. E-mail: morten.andersen@mq.edu.au

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Supplementary Figures Legends

Supplemental Figure 1 Example of N-glycan isomeric separation by PGC and MSMS fragment-specific substructure diagnostic ions. A) Distinct PGC-LC elution pattern for α2,6 and α2,3 sialic acid and fragment-specific substructure diagnostic ions for core fucosylation and 6 arm composition. B) Fragment-specific substructure diagnostic ions for LacdiNac containing N-glycans. C) Fragment-specific substructure diagnostic ions for bisecting containing N-glycans. D) Fragment-specific substructure diagnostic ions for NeuGc containing N-glycans.

Supplementary Figure 2 Overview of the reproducibility of unique glycoform identified in the prostate tissue. A) Distribution of (number) and % of unique glycoforms identified across 10-100% of the 54 files. The numbers in parenthesis show the number of glycoforms. B) Distribution of (number) and % of unique glycoforms identified across 1-6 conditions (five Pca grades and BPH) is shown in the bar graph.
**Supplementary Tables Legends**

Supplemental Table SA: Clinical information of the patients included in the study

Supplementary Table SB: Overview of the raw files and search parameters.

Supplementary Table S1: N-glycome dataset of PCa and BPH tissues.

Supplementary Table S2: O-glycome dataset of PCa and BPH tissues.

Supplementary Table S3: Intact N-glycopeptide dataset of PCa and BPH tissues.

Supplementary Table S4: Intact O-glycopeptide dataset of PCa and BPH tissues.

Supplementary Table S5: De-N-glycopeptide dataset of PCa and BPH tissues.

Supplementary Table S6: Proteome dataset of PCa and BPH tissues.

Supplementary Table S7: Significant correlated intact N-glycopeptide with N-glycan structure.

Supplementary Table S8: Significant correlated intact O-glycopeptide with O-glycan structure.

**Supplementary Data Legends**

Supplementary Data S1: Spectra evidences for reduced N-glycans (alditols) released from PCa and BPH tissues

Supplementary Data S2: Spectra evidences for reduced O-glycans (alditols) released from PCa and BPH tissues
Supplementary Figures

Supplementary Figure S1

A

B

Full MS Base Peak
m/z=1059.4

MS/MS spectra
m/z=1059.38
RT 30.52 min
Supplementary Figure S2

A

B

% of unique glycoforms

Frequency of observation (%)

% of unique glycoforms

Frequency of observation (%)

(30) 0.4 (1142) 15.3 (789) 10.6 (691) 9.3 (689) 9.3 (1223) 16.4

(5) 0.0 (7) 0.1 (9) 0.1 (11) 7.1 (530) 92.5 (6887)