

A Transition Metal Carbonyl Probe for Use in a Highly Specific and Sensitive SERS-Based Assay for Glucose

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S Supporting Information

ABSTRACT: A triosmium carbonyl cluster–boronic acid conjugate is used as a secondary carbohydrate probe in a SERS-based assay. The assay does not require conjugation of the metal carbonyl probe to a SERS-active species, and it utilizes the CO stretching vibrations of the metal carbonyl, which lies in a silent region of the SERS spectrum (1800–2200 cm⁻¹), for quantification. High selectivity for glucose over fructose and galactose is obtained, and a human urine sample doped with glucose is detected accurately.

Biological markers find importance in a vast number of applications in both biology and the biomedical sciences. Among the most commonly employed are radio-labeled and fluorescent compounds. Associated with the former are all the hazards surrounding the handling of radioactive materials; the latter often suffers from interference by fluorescent biological materials. The development of new biological markers thus continues to be of interest. One promising area of development for biological markers is that based on compounds that absorb or emit in the mid-infrared. Of particular interests are transition metal carbonyl compounds, i.e., organometallic compounds containing CO as ligands. This class of compounds has already found applications in the biomedical field, including biological immunoassay (metalloimmunoassay), pharmaceuticals, CO-therapy (CO-release molecules), and bioimaging,^{1–15} and a useful characteristic is their strong CO stretching vibrations in the mid-IR (1800–2200 cm⁻¹); this region of the mid-IR spectrum is a spectral window in living systems.

The use of organometallic compounds as biological markers began with the work of Jaouen et al., who demonstrated their use as such, particularly for the estrogen receptors.^{1–3,16–19} One limitation which hampered their use is the poor spatial resolution for the mid-IR, about 6 μm, which implies that they cannot be used for intracellular imaging except with an elaborate setup.¹⁵ Another is the interference of the strong absorption at ~1600 cm⁻¹ of water, which tails into the CO stretching vibration region. This will be especially important when working with biological samples. A solution to these two limitations, however, were demonstrated recently through the use of metal carbonyl–nanoparticle conjugates (OM-NP).²⁰ This made use of the

phenomenon of surface-enhanced Raman scattering (SERS), which leads to a dramatic improvement in the inherently low sensitivity of Raman signals.^{21–23} In this technique, the Raman signals of molecules deposited onto a nanostructured surface can be enhanced by several orders of magnitude (typically 10⁶ to 10¹⁴) due to interactions with the strong surface plasmon resonance of the surface.^{24,25} By moving to Raman detection, the spatial resolution is improved tremendously as the excitation radiation used in Raman microscopy is in the visible region, and interference from water is bypassed. SERS has also been successfully adapted for other chemical sensing applications, resulting in higher detection limits,^{23,26–28} including DNA detection,^{29–31} cancer diagnosis,³² and cellular molecules detection.³³ We wish to report here that metal carbonyl conjugates can also be developed into a biological probe even without direct conjugation onto a nanoparticle. In particular, we will demonstrate their use in a SERS-based assay for glucose.

According to the World Health Organization (WHO) report for 2012, diabetes affects 371 million people worldwide. There is a direct association of blood glucose level with this metabolic disorder, and hence great effort has been made in the development of glucose sensors.^{34–41} SERS-based direct sensing of glucose, however, remains highly challenging.⁴² The problem of the inherently poor Raman cross section of the glucose molecule can be partially circumvented via the use of a carbohydrate recognition molecule, such as boronic acid, to capture the glucose onto a nanostructured surface. This increases the concentration of glucose on the surface and hence improves the detection sensitivity.⁴³ Unfortunately, the SERS spectrum of glucose and of the functional groups on the carbohydrate recognition molecule, such as the boronate (1370 cm⁻¹) and aromatic (1580 cm⁻¹) groups in 4-mercaptophenylboronic acid, lie in the 400–1800 cm⁻¹ region. This region suffers from interference by absorption bands of biomolecules,^{44–46} which limits the detection of glucose or even the recognition molecule.

Our procedure for the SERS detection of glucose utilizes a sandwich assay in conjunction with a metal carbonyl probe. The principle of the assay is based on the ability of glucose to form a bidentate glucose–boronic complex which is unique to glucose; most of the other physiologically relevant carbohydrates bind to

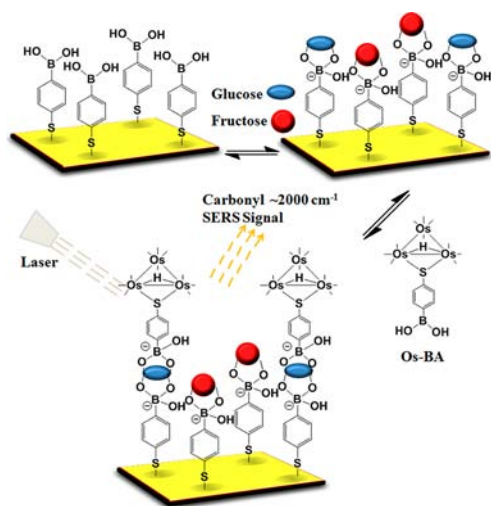
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boronic acid as monodentate complexes.^{47–59} Two carbohydrate receptors are used; the first (primary) receptor comprises 4-mercaptophenylboronic acid (BA) anchored onto a SERS substrate, and the second (secondary) receptor is a 4-mercaptophenylboronic acid–triosmium carbonyl cluster conjugate (Os-BA). Glucose is first captured by the primary carbohydrate receptor, followed by labeling by the Os-BA. In this way, it is possible to selectively quantify the concentration of glucose via the CO stretching vibrations which are enhanced by the SERS substrate.

The SERS-active substrate used is Bimetallic Film Over Nanospheres (BMFON).⁶⁰ This is an in-house fabricated substrate comprising a multiple nanostructure formed by depositing polystyrene onto a glass slide prior to gold and silver sputtering to impart a gold–silver coat. It does not require a clean room environment or sophisticated instruments for fabrication, and can give excellent signal enhancement of Raman signals; it has been employed in the detection of biomolecules within an extremely low sample volume ($\sim 20 \mu\text{L}$).⁶¹ The BA is immobilized onto BMFON via its thiol ($-\text{SH}$) group, and its boronic acid group ($\text{B}(\text{OH})_2$) functions as the carbohydrate receptor (Scheme 1); this eliminates the need to introduce the

Scheme 1. Schematic for the Fabrication of BA-Functionalized BMFON^a



^aA glucose molecule brings Os-BA to the substrate via formation of a bidentate complex. Inset image: photograph of BMFON.

carbohydrate receptor and the substrate-binding moiety separately. The distribution of BA prior to introduction of glucose was first examined by SERS mapping using an absorption peak of the phenyl group at 1580 cm^{-1} , which shows an even distribution of BA on BMFON (Figure 1). The BA layer is very stable; the substrate soaked in phosphate buffered saline (PBS) showed no significant variation in the signals and distribution of BA over a period of 3 days (Figure 1c–e).

The secondary carbohydrate receptor Os-BA is a triosmium carbonyl cluster conjugate. Osmium carbonyl clusters are often air- and moisture-stable, and they have been shown to be sufficiently robust in bioimaging applications.⁸ Os-BA was prepared by the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with 4-mercaptophenylboronic acid to form the $\mu, \kappa\text{S}$ -thiolate bridged cluster (Scheme 2), and has been completely characterized spectroscopically by IR, HR-MS, and ^1H and ^{13}C NMR (Figures S1–S4). A sample of Os-BA incubated with an excess of glucose

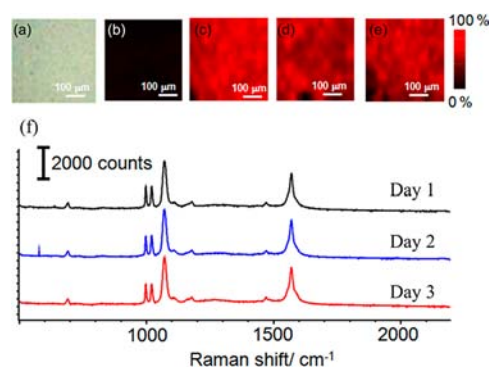
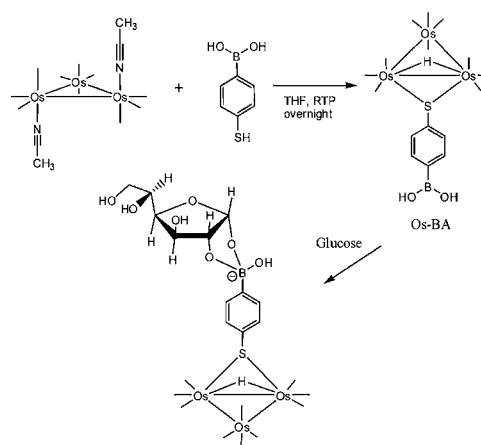


Figure 1. (a) Bright field image of BMFON. SERS mapping images at 1580 cm^{-1} before (b) and after (c) immobilization of BA. Stability test of BA-functionalized BMFON in PBS solution: SERS mapping images at 1580 cm^{-1} on (c) day 1, (d) day 2, and (e) day 3. (f) SERS spectra of BA-functionalized BMFON from days 1–3.

Scheme 2. Synthesis of Os-BA and Its Reaction with Glucose^a



^aThe short lines extending from Os represent carbonyl (CO) ligands.

at pH 9.0 showed the presence of an adduct of Os-BA with glucose in the HR ESI-MS (Scheme 2 and Figure S5), demonstrating its ability to bind glucose.

Fructose and galactose are the most abundant monosaccharides after glucose.^{62–64} There have been numerous reports that utilized the ability of glucose to form complexes with diboronic acids for the selective sensing of glucose over other saccharides.^{47–49,65,66} Most of these, however, make use of molecules containing two boronic acid groups; the formation of a stable boronic acid–diol complex requires the presence of syn-periplanar hydroxyl groups for preferential binding,^{66–69} and these diboronic acids are designed to straddle the two sets of syn-periplanar diol groups present in the α -D-glucopyranose ring.^{68,69}

BA-functionalized BMFON incubated with a small amount ($\sim 20 \mu\text{L}$) of a solution of glucose, fructose, or galactose prior to treatment with Os-BA shows significant CO stretching vibrations at $\sim 2000 \text{ cm}^{-1}$ only with glucose; it is very modest with fructose or galactose (Figure 2). The intensity of the sharp peak at 2111 cm^{-1} as a function of concentration, after incubation with varying concentrations of the three carbohydrates, shows that the SERS signal intensity increases as a function of the concentration of glucose (Figure 3); the limit of detection is estimated at 0.1 mM , with a detection range (0.1 – 10 mM) that covers the physiological concentration (5 mM). This detection limit compares very well with a similar glucose assay

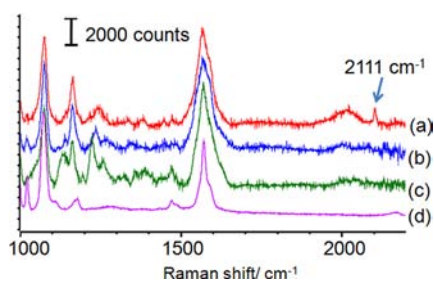


Figure 2. Raman responses for BA-functionalized BMFON incubated with 1 mM of (a) glucose, (b) fructose, (c) galactose, and (d) control, prior to incubation with Os-BA.

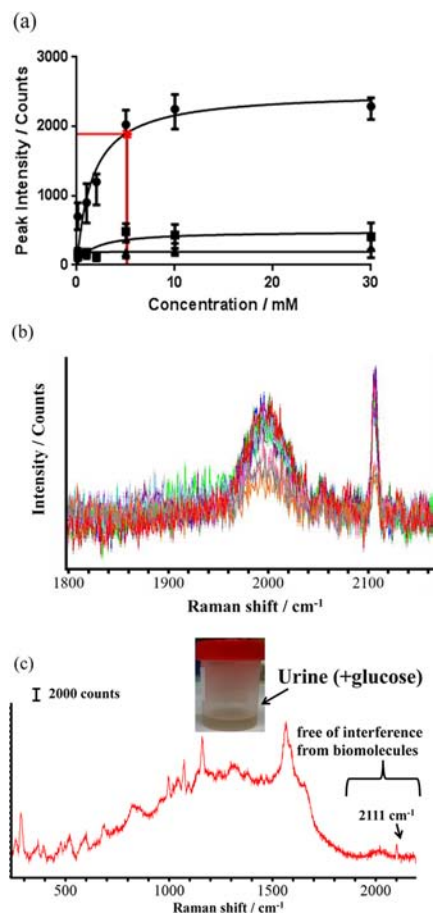


Figure 3. (a) Plot represents the intensity of CO stretching frequency versus different concentrations of (●) glucose, (▲) fructose, and (■) galactose, with the interpolated value for the spiked urine sample shown in red. The first data points are at 0.1 mM. (b) SERS spectrum of Os-BA obtained from different concentrations of glucose. (c) SERS spectrum of Os-BA after BMFON has been incubated with a urine sample spiked with glucose.

which also utilized BMFOM and had a detection limit of 5 mM,⁴² as well as another which utilized nanoparticles and a detection limit of 0.33 mM.⁷⁰ The dissociation constants (K_D) were calculated to be 1.9 mM for glucose, compared to 5.3 and 23 mM for galactose and fructose, respectively. Clearly Os-BA has a much greater affinity for glucose than for fructose and galactose; the lower K_D values for fructose and galactose can be attributed to their lower tendency to form bidentate complexes.⁶⁵ The selectivity observed is reminiscent of a recent report which utilized the greater affinity of fructose for binding to

monoboronic acids and of glucose to form 1:2 adducts.⁵⁹ Presumably, therefore, all three carbohydrates interacted with the BA-functionalized BMFON, but there is preferential binding of Os-BA with the surface-bound glucose.^{71,72}

Glucose monitoring for diabetes is usually carried out on urine or blood samples; the former is not a substitute but rather an alternative or complement, which can provide very valuable information where blood glucose monitoring is not accessible, affordable, or desirable. To demonstrate the potential practicality of our sensor system, we determined glucose in urine samples spiked with a standard glucose solution (Figure 3c). The concentration of glucose in the urine sample was determined to be 5.1 mM, in good agreement with the amount of glucose added (5.0 mM).

In conclusion, we have demonstrated the use of a triosmium carbonyl cluster–boronic acid (Os-BA) conjugate as a mid-IR probe in a novel assay for glucose. Compared with other glucose detection methods reported in the literature, this glucose assay exhibits several advantages. First, no prior purification of the sample is needed. Second, an extremely low sample volume is required. Third, it shows very high specificity for glucose. Lastly, the spectroscopic handle for glucose quantification is in a spectral window (1800–2200 cm^{-1}) which is relatively devoid of interference from any functional groups of biomolecules. Given this combination of advantages, we expect that metal carbonyls as biological probes will find wide applicability, and this concept for a glucose assay presented here can be developed into a clinical diagnostic tool.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and supporting data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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