Supporting Information - Figure-of-merit characterization of hydrogen-bond acidic sorbents for waveguide-enhanced Raman spectroscopy

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Abstract

This article contains supporting information relevant to the manuscript "Figure-of-merit characterization of hydrogen-bond-acidic sorbents for waveguide-enhanced Raman spectroscopy." First, we describe the synthesis procedures of the sorbent materials mentioned in the manuscript. We then discuss the noise sources present in our spectra and their impact on the measured detection limit. Finally, the calculation of the sorbent figure of merit is discussed.
PMBTTS synthesis

Poly(methyl 2-butanol, 1,1,1-trifluoro-2-(trifluoromethyl))siloxane (PMBTTS) is a carbosilane chain polymer identical in structure to the polymer described in Wang et al., but synthesized via the following procedure (depicted in Fig. S1). First, 2-vinylhexafluoroisopropanol and diethoxy(methyl)silane were reacted (with sodium metal and benzophenone) with THF. The reaction flask was then flushed with dry nitrogen for fifteen minutes and refluxed with platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane for 24 hours. The reaction was cooled and vacuum-filtered through diatomaceous earth and activated charcoal. The resulting functionalized monomer was heated to 80 °C glacial acetic acid for fifteen hours. Afterwards, the reaction was diluted in hexanes and washed with nanopure water repeatedly, until the resulting aqueous layer was neutral. The hexane layer was then dried with anhydrous sodium sulfate, vacuum filtered and the solvent was removed under vacuum.

![Figure S1: PMBTTS Synthesis](image)

o1pBPAF synthesis

Previously developed HB acidic sorbent polymers, while chemoselective for analytes of interest, have suffered from undesirable intermolecular sorbent-sorbent hydrogen-bonding (also known as sorbent self-association). Our recent sorbent development efforts have focused on synthesizing HB acidic fluorinated bisphenol derivatives designed to limit sorbent self-association. These derivatives are based on differing substituents positioned ortho- to the phenolic hydroxyl denoted by the “R” and “R1” groups in Fig. S2.
“R” represents either alkyl or silyl substituents, whereas “R1” represents hydrogen, the same alkyl group as “R”, or a different alkyl group than “R”. The “R” and “R1” groups vary in size and steric bulk and shield the phenolic −OH from hydrogen-bonding to other sorbent molecules while allowing the smaller analyte molecules to approach the −OH sites and form hydrogen bonds. The ideal sorbent will have “R” and “R1” groups that form an exclusive binding pocket for the analyte while blocking sorbent self-association.

Figure S3 illustrates the synthesis of the bisphenol sorbent o1pBPAF. This procedure was adapted from that of Abraham, et al. Bisphenol AF undergoes a bis-allylation to form the bis-allyl ether, followed by a Claisen rearrangement at high temperature to yield the C-allylated bisphenol. This intermediate the undergoes hydrogenation to give the final product.
Measurement noise

The InGaAs detector on our spectrometer (Princeton Instruments Pylon IR) has two sources of “dark” noise: Readout noise, which is independent of exposure time; and dark signal noise, which is shot noise arising from the dark signal. According to the manufacturer’s specifications, the readout noise is 400 electrons (e−), the dark signal is 3200 electrons per second (e−/s), and the gain, G, is 75 electrons per count (e−/ct).

The readout noise, RN, then is given by

\[
RN = \frac{400e^-}{G} = 5.3 \text{ cts} \tag{S1}
\]

The dark signal noise, DN, is the square root of the number of dark electrons detected in an exposure time:

\[
DN = \sqrt{3200(e^-/s) \tau G} = 7.5 \text{ cts} \tag{S2}
\]

where τ is the exposure time, which is 100 s for the measurements reported here.

The background signal from WERS (BG) will also contribute optical shot noise (SN) to the measurement. Typical background signal at the wavelength of the primary DMMP Raman peak (1150 nm) is 10 cts/s. Since the optical shot noise is also given by the square root of the photon number, it is given by:

\[
SN = \sqrt{\frac{BG \tau G QE}{QE G}} = \sqrt{\frac{10(cts/s) \tau QE}{G}} = 3.4 \text{ cts} \tag{S3}
\]

where QE is the detector quantum efficiency, approximately 0.85% at 1150 nm. Adding the noise in quadrature, including the readout noise and dark noise twice to account for the dark spectrometer exposure and signal exposure, gives a total measurement noise of

\[
\sqrt{2RN^2 + 2DN^2 + SN^2} = 13.4 \text{ cts} \tag{S4}
\]
This is comparable to the measured noise ($\sim 20$ cts) in our 100 s exposures, showing that background shot noise is a significant, though not dominant, source of total measurement noise.

**Figure of merit**

The figure of merit (FOM) for the sorbent films discussed in this manuscript can be described by the following:

$$\text{FOM}(\lambda) = K(\lambda) \frac{\alpha_{\text{SiO}_2}(\lambda) \sqrt{BG_{\text{SiO}_2}(\lambda)}}{\alpha_{\text{sorb}}(\lambda) \sqrt{BG_{\text{sorb}}(\lambda)}}$$

where $K$ is proportional to the the partition coefficient, here taken as the slope of peak height vs. DMMP concentration from Fig. 6 of the manuscript. $\alpha$ is the loss, in cm$^{-1}$, of the waveguide, and $BG$ refers to the background signal (Raman and/or fluorescence) measured when there is no analyte present. Implicit in this normalization is the assumption that the sorbent refractive indices are all similar to that of SiO$_2$, since normalization assumes equivalent modal overlaps with the top cladding. A complete analysis of the sorbent refractive index is outside the scope of this work, but our preliminary measurements show the sorbent’s indices to vary by no more than 0.03 from that of SiO$_2$. Calculations of modal overlaps and WERS $\beta$-factors show that this variation does not significantly affect the figure of merit ($< 20\%$). Shown below are measurements in the near-infrared of the refractive index of three of the sorbents studied here, as well that of the PECVD SiO$_2$ used for the reference top cladding.

The propagation loss used to calculate $\alpha$ in Eq. S5 is shown in Fig. 3 in the manuscript. The length of the waveguide used to measure the limit of detection is accounted for, which allows for a comparison of sorbents even if they are deposited on spirals of varying lengths. Shot noise, a significant source of our measurement noise as described above, is accounted for by taking the square root of the spectrum intensity when no analyte is present. As described above, the total measurement noise will contain contributions from the detector.
Figure S4: Preliminary NIR measurements of the sorbent’s refractive index. Also shown are measurements and reference values of SiO\textsubscript{2}. 
as well as the background shot noise, but in order to evaluate the sorbent-specific FOM, only the optical background should be considered. This collection of factors, \( \alpha(\lambda) \sqrt{BG(\lambda)} \), is calculated for each sorbent film, as well as for a waveguide clad in SiO\(_2\). To separate the Raman background and loss of the sorbent from the core or bottom cladding material, we normalize the sorbent loss and shot noise to that of an SiO\(_2\)-clad waveguide. Figure S5 shows the normalized denominator spectra for each sorbent.

![Figure S5: Denominator of the FOM as a function of wavenumber for each sorbent.](image)

The only remaining parameter to describe the sorbent performance is the partition coefficient, which can be inferred by exposing the sorbent to varying concentrations of an analyte (DMMP in this work, at \( \lambda = 1150 \text{ nm} \)) and recording the peak height. The slope of peak height versus analyte concentration \( (K) \) is proportional to the partition coefficient. This fac-
tor defines the numerator of the FOM, such that a higher coefficient indicates better sorbent performance.

References

