

Electronic Supplementary Information

Water Soluble Cucurbit[6]uril Derivative as a Potential Xe Carrier for ^{129}Xe NMR-Based Biosensors

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Materials. All the chemicals were of reagent grade and used without further purification. CB*[6] was prepared as described in the literature.¹ Xenon gases (5 % and 99.999 %) were purchased from PS CHEM CO., LTD.

^{129}Xe NMR Spectroscopy. All ^{129}Xe NMR experiments were performed at 295 K on a Bruker Avance 300 spectrometer (83.02 MHz for ^{129}Xe frequency) equipped with a super-widbore magnet and 10 mm broadband probe, and chemical shifts were referenced to the free xenon gas at 0 ppm. For ^{129}Xe NMR experiments, xenon aqueous solution was prepared using the 5 % xenon gas mixture. The concentrations of xenon are 0.83 mM in the water and 0.76 mM in the Na_2SO_4 solution.

Production of Hyper-polarized (HP) ^{129}Xe gas. HP xenon gas was prepared through the spin-exchange method using Rubidium (Rb) in a closed continuous flow home-built optical pumping (OP) system, a modified system as reported in the literature.² The HP xenon gas was supplied continuously from OP cell through a 1/16 inch Teflon tubing to bubble into the sample solution in NMR magnet. The flow rate was monitored with a flow meter (KOFAC) and kept constant 30~35 mL/min. The polarization of HP xenon in gas was ca. 5~10 %.

2D exchange NMR experiments. 2D ^{129}Xe EXSY spectra were recorded at various mixing times (τ_m) with 2048 data points along t_2 domain and 64 data points along t_1 domain using States-TPPI method in t_1 dimension with a relaxation delay of 5 s. To evaluate the rate constants, we used the equation (1) and (2) as described in the literature,³ where $k = k_{AB} + k_{BA}$.

$$k = \frac{1}{\tau_m} \ln \frac{r+1}{r-1} \quad (1)$$

$$r = \frac{4X_A X_B (I_{AA} + I_{BB})}{(I_{AB} + I_{BA})} - (X_A - X_B)^2 \quad (2)$$

The r is the integrated volume ratio of cross signal and diagonal signals for asymmetric two-site chemical exchange with mole fraction X_A and X_B .

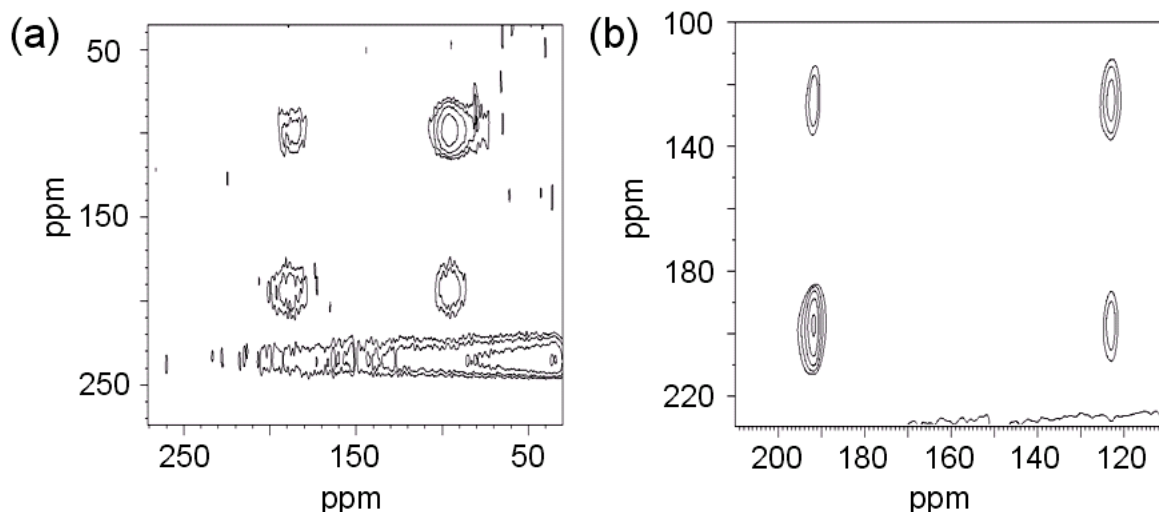


Figure S1. 2D ^{129}Xe exchange (EXSY) spectra of xenon in the presence of 3 equiv CB*[6] with the mixing time of 2 ms (a) in pure water and (b) in 0.2 M aqueous Na_2SO_4 solution at 295 K.

Isothermal Titration Calorimetry (ITC). The formation constant and thermodynamic parameters for the inclusion of xenon in CB*[6] were determined by titration calorimetry using a VP-ITC instrument from MicroCal, Inc. All solutions were prepared in purified water (Milli-Q, Millipore). The CB*[6] solution was degassed prior titration experiment according to procedures provided by MicroCal, Inc. A solution (0.10 mM) of CB*[6] was placed in the sample cell (1.398 mL). As 4.74 mM solution of xenon was added in a series of 20 injections (14 μL), the heat evolved was recorded at 295.15 K. The data were analyzed and fitted by the Origin software adapted for ITC data analysis (MicroCal, Inc).

Saturated Aqueous Xenon Solution for ITC Experiments.⁴ Saturated aqueous xenon solution was prepared at 295 K. Deionized water was added to a round-bottom flask, which was then capped with a septum and bubbled with high purity argon gas via a 22 gauge needle reached to the bottom of the flask for 20 minutes. Excess pressure was vented by a 26 gauge needle. Degassing process was carried out by high vacuum via a 22 gauge needle inserted through the septum into the headspace of the flask for 5 minutes. If the water was bubbled violently, active pumping was momentarily switched to passive vacuum. When the vacuum degassing was completed, the flask was bubbled with pure xenon (99.999 %) for 5 minutes by same procedure as argon bubbling. Then, the vent needle and purging needle were removed. A syringe tube attached to a latex balloon filled with xenon gas was inserted through the septum into the headspace of the flask via a 22 gauge needle. The excess pressure of xenon was then vented by a 26 gauge needle until the gas pressure inside the flask reached 101.325 kPa (1 atm).

Calculation of Aqueous Xenon Concentration. The mole fraction (χ) of xenon in pure water at 101.325 kPa partial pressure was calculated by Rubin Battino based on the data of three workers.⁵ The fitting equation used was

$$\ln \chi = A + B/(T/100 \text{ K}) + C \ln (T/100 \text{ K}) + DT/100 \text{ K} \quad (3)$$

Using $T/100 \text{ K}$ as the variable rather than T/K gives coefficients of approximately equal magnitude. The best fit for 20 data points was

$$\ln \chi = -74.7398 + 105.210/(T/100 \text{ K}) + 27.4664 \ln (T/100 \text{ K}) \quad (4)$$

where χ is the mole fraction solubility of xenon at 101.325 kPa partial pressure of gas.

The definition of the mole fraction solubility of xenon $\chi(\text{Xe})$ for this binary system is given by:

$$\chi(\text{Xe}) = n(\text{Xe})/[n(\text{Xe}) + n(\text{H}_2\text{O})] \quad (5)$$

(n(Xe): the mole number of xenon, n(H₂O): the mole number of water)

The maximum value of $\chi(\text{Xe})$ at 295.15 K is calculated by equation (4) as 8.556×10^{-5} .

The concentration of water at 295.15 K was determined by following calculation

$$\begin{aligned} \text{Density of water at 295.15 K} &= 0.9977735 \text{ g/cm}^3 \\ n(\text{H}_2\text{O}) &= (997.7735 \text{ g/cm}^3)(\text{cm}^3/\text{L})(\text{mol}/18.015\text{g}) = 55.386 \text{ mol/L} \end{aligned}$$

In a 1 liter system, n(H₂O) of equation (5) can be substituted by the value of 55.386 mol based on the assuming that xenon saturation does not significantly change the volume of the water. After insertion of the value of $\chi(\text{Xe})$ and n(H₂O), equation (5) divided by L to give:

$$n(\text{Xe})/L = (8.556 \times 10^{-5}) \times [n(\text{Xe})/L + 55.386 \text{ mol/L}] \quad (6)$$

The equation (6) is calculated to:

$$n(\text{Xe})/L = (8.556 \times 10^{-5}) \times 55.386 \text{ mol/L}/(1 - 8.556 \times 10^{-5}) = 4.74 \text{ mmol/L}$$

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