Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

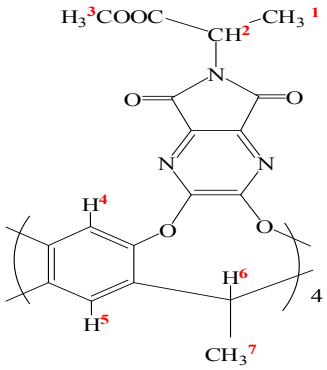
Resorcinarene-based cavitands with chiral amino acid substituents for chiral amine recognition

Na Li, Fan Yang, Hillary A Stock, David V. Dearden, John D. Lamb, and Roger G. Harrison*

Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA.

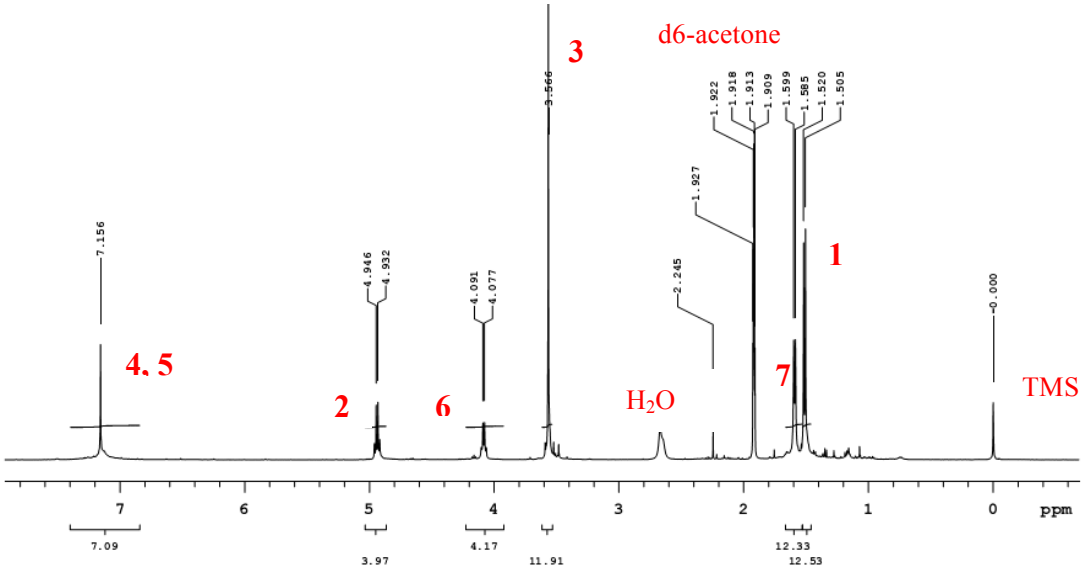
Tel.: 801 422-8096; Fax: 801 422-0153; E-mail: roger_harrison@byu.edu

Characterization of AME, AMNa, and AMA

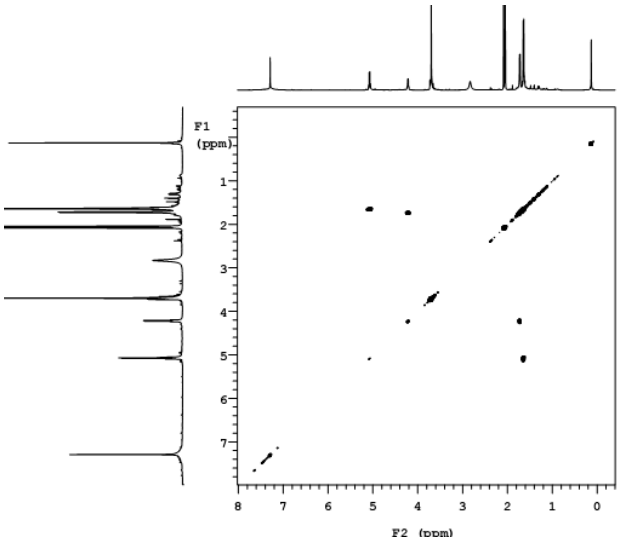


The structure of AME

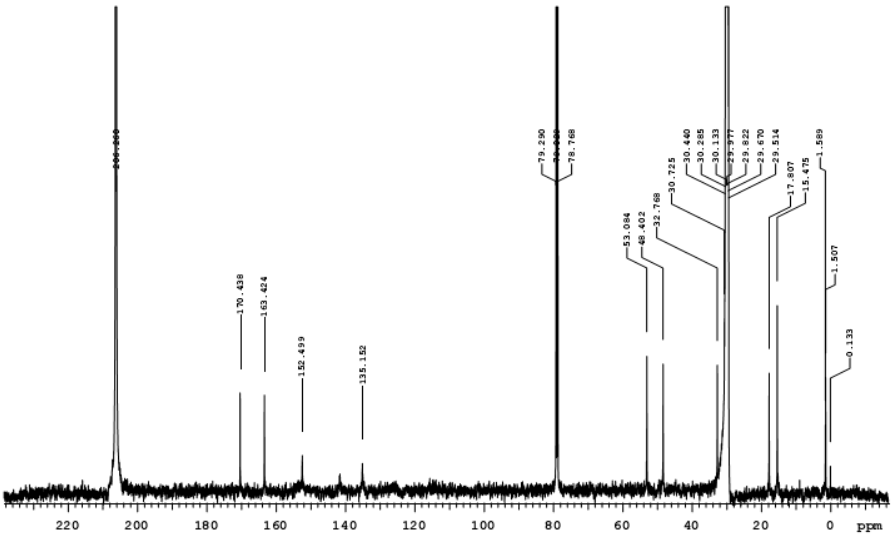
1. ^{1}H NMR structure of AME in d_6-acetone.



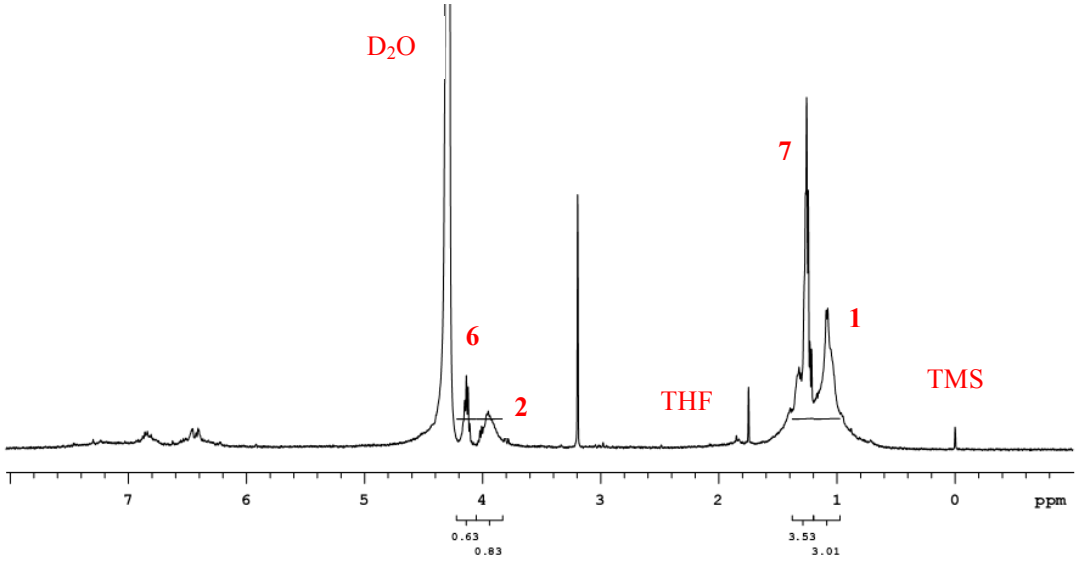
2. 2D COSY of AME in d_6-acetone.



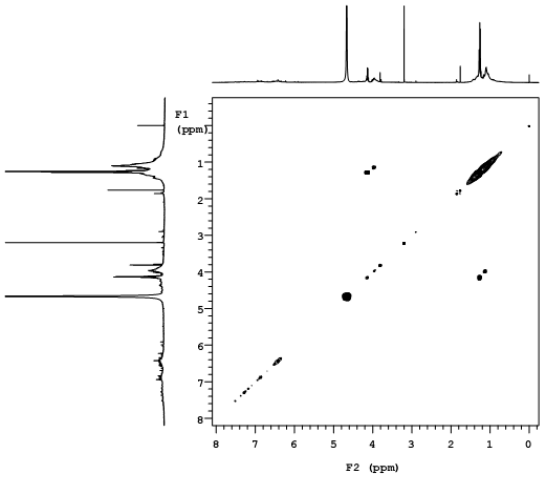
3. ^{13}C NMR of AME in d_6-acetone.



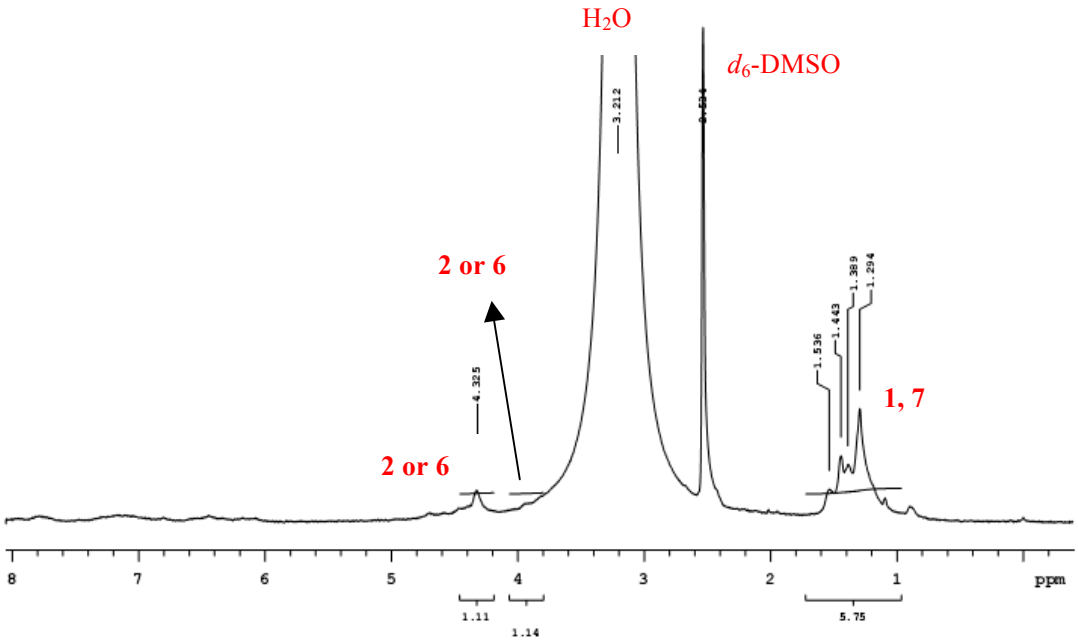
4. ^{1}H NMR spectrum of AMNa in D_2O at 60 ^{o}C.



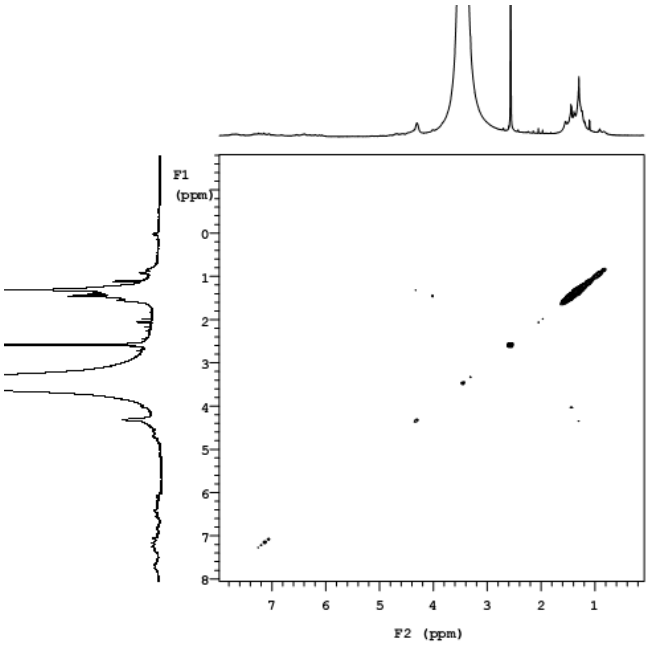
5. 2D COSY of AMNa in D_2O.



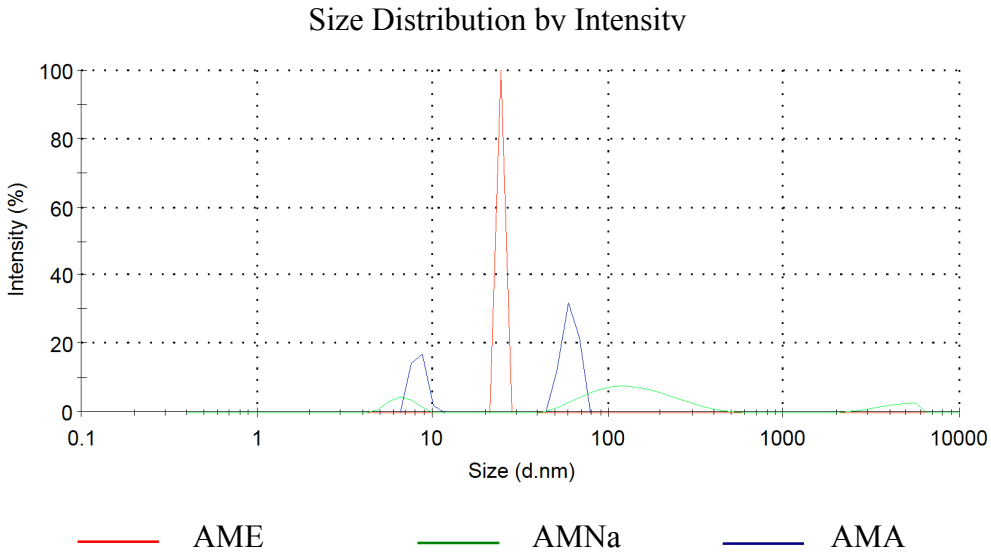
6. ^{1}H NMR spectrum of AMA in d_6-DMSO at 80 ^{o}C.



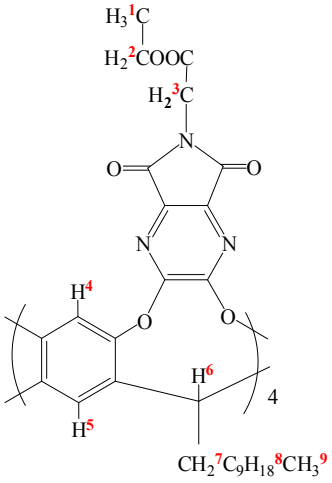
7. 2D COSY of AMA in d_6-DMSO.



8. Particle size comparison between AME, AMNa, and AMA.

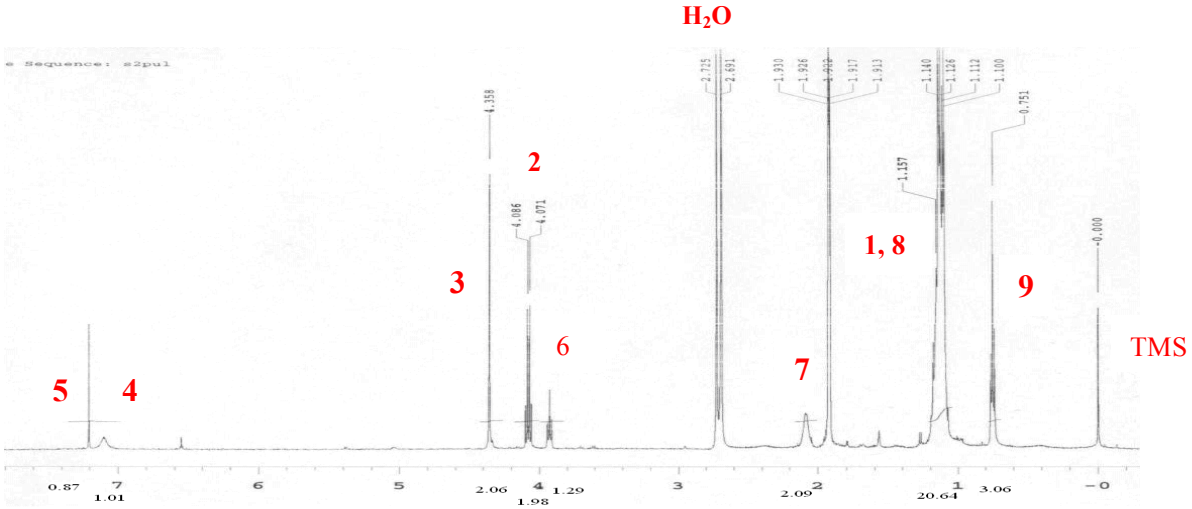


Characterization of GUE, GUNa, and GUA



The structure of GUE

1 ^{1}H NMR structure of GUE in d_6-acetone.



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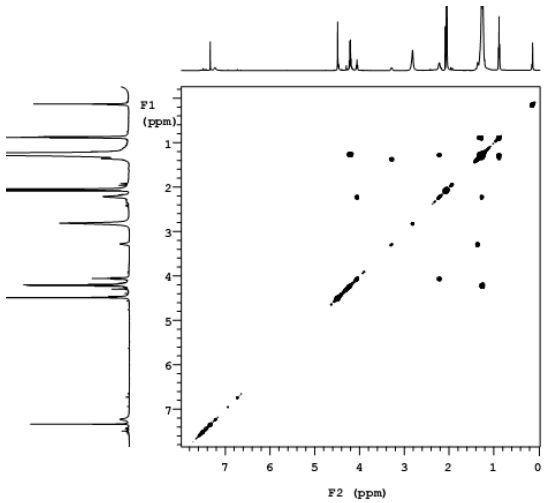
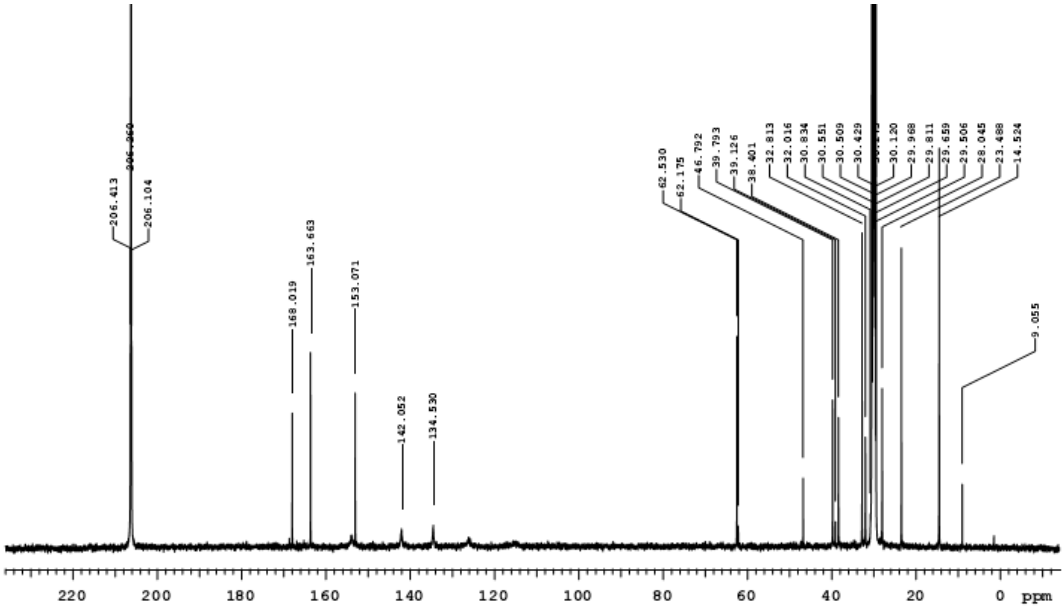
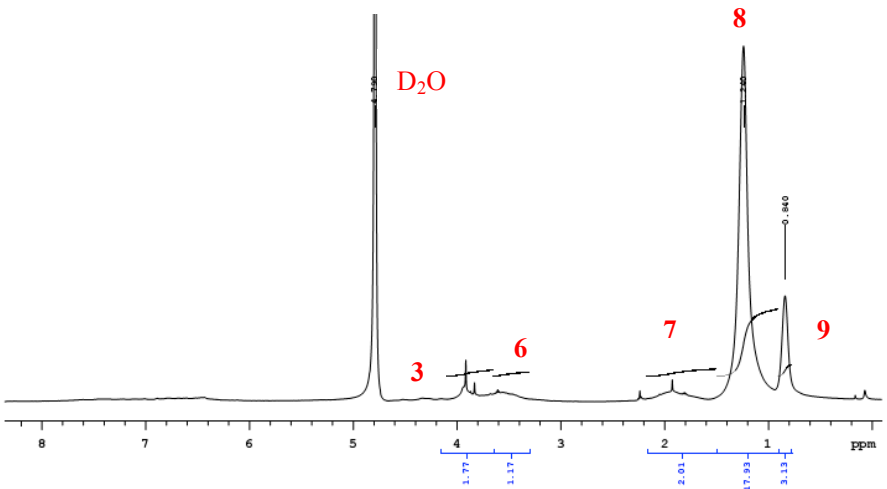
2D COSY of GUE in d_6-acetone



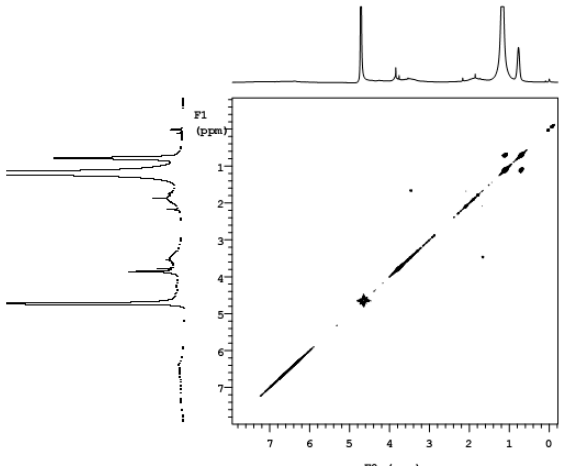
3 ^{13}C NMR of GUE in d_6-acetone.



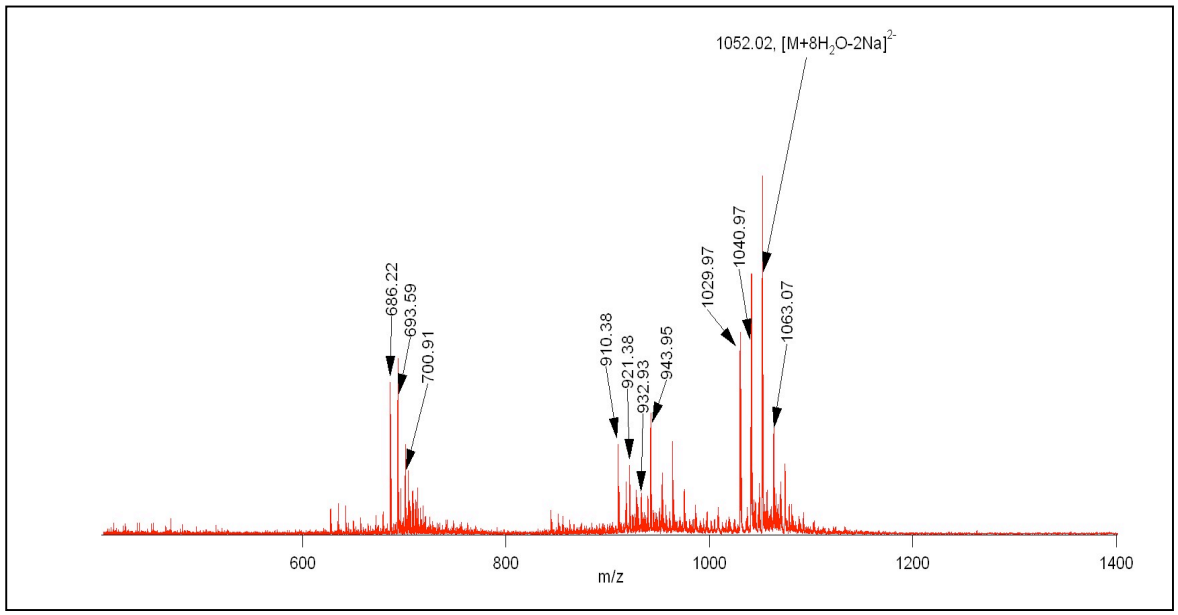
4. ^{1}H NMR of GUBNa in D_2O.



5. 2D COSY of GUNa in D_2O.

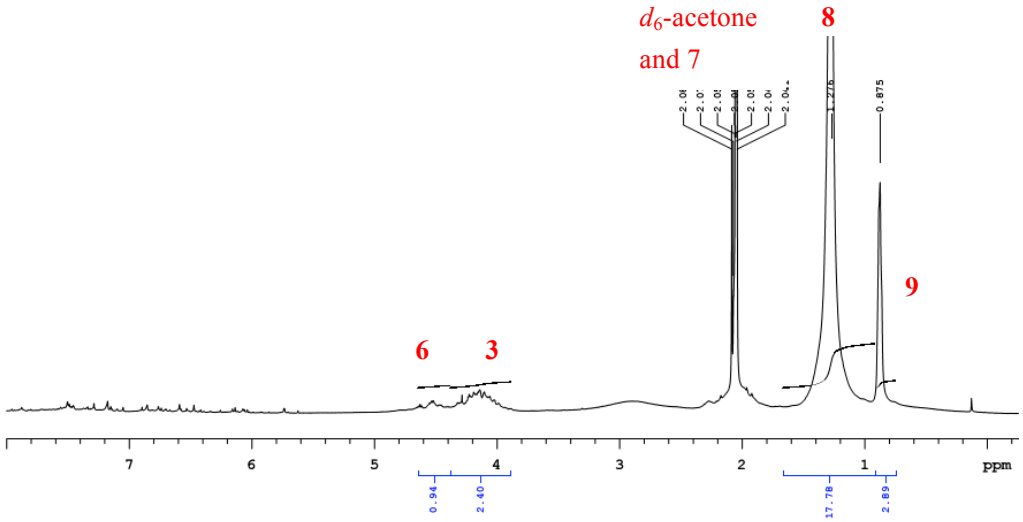


6. FTICR-MS of GUNa (M = GUNa).

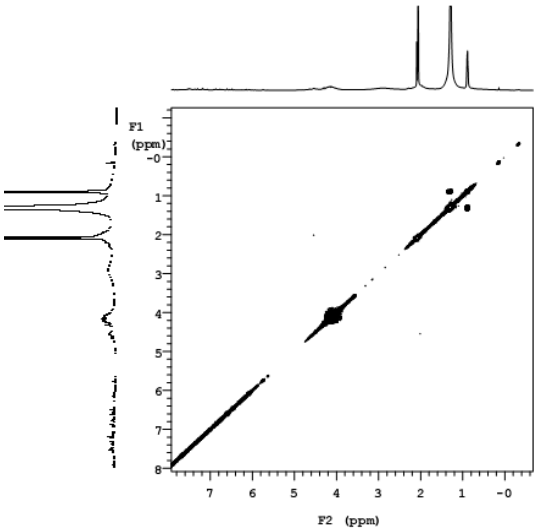


M = GUNa; $[M+8H_2O-2Na]^{2-}$ = 1052.02 (calculated: 1052.07); $[M+8H_2O-Na-H]^{2-}$ = 1063.06; $[M+8H_2O-3Na+H]^{2-}$ =1040.97; $[M+8H_2O-4Na+2H]^{2-}$ =1029.97; $[M+8H_2O-3Na-1Arm+H]^{2-}$ =1040.97; $[M+8H_2O-2Na-1Arm]^{2-}$ = 921.38; $[M+8H_2O-Na-1Arm-H]^{2-}$ = 932.93; $[M+8H_2O-1Arm-2H]^{2-}$ = 943.95; $[M+8H_2O-3Na-1Arm+H]^{2-}$ = 910.38; $[M+8H_2O-3Na]^{3-}$ = 693.68; $[M+8H_2O-4Na+H]^{3-}$ =1686.22; $[M+8H_2O-2Na-H]^{3-}$ = 700.91.

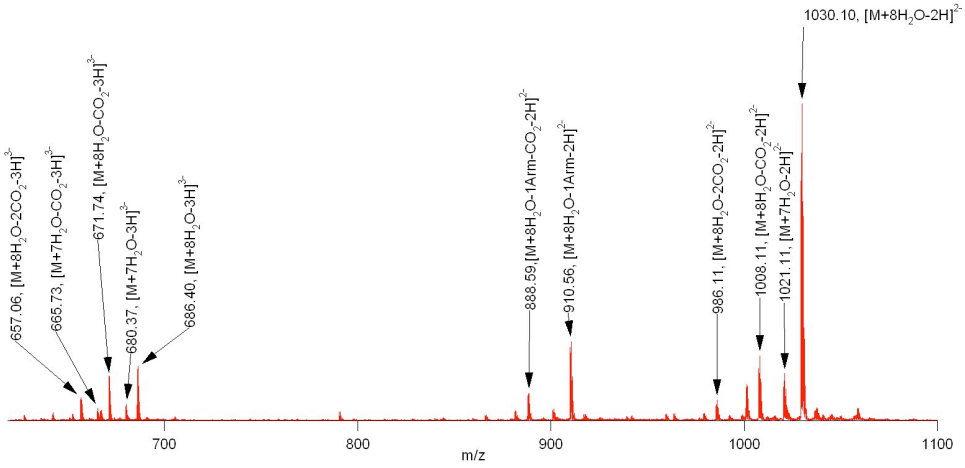
7. ^{1}H NMR of GUA in d_6-acetone.



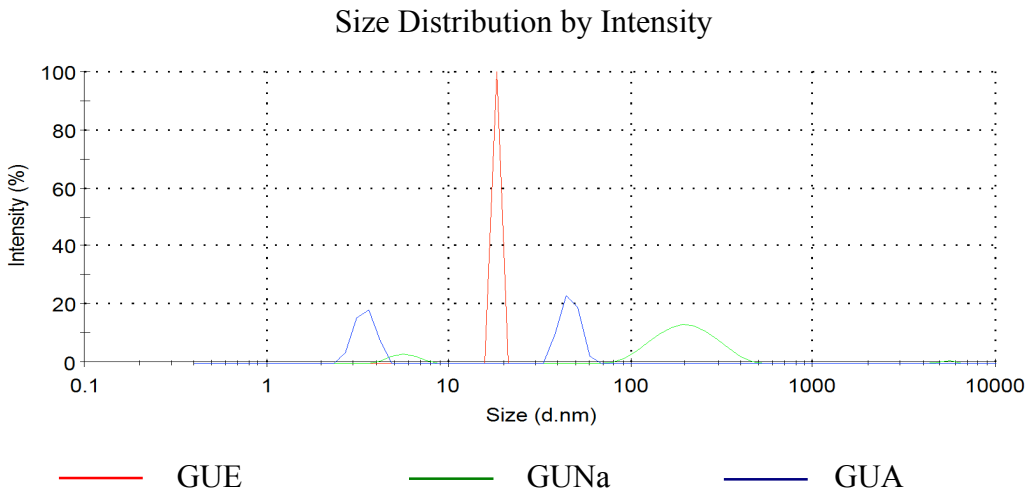
8. 2D COSY of GUA in d_6-acetone.



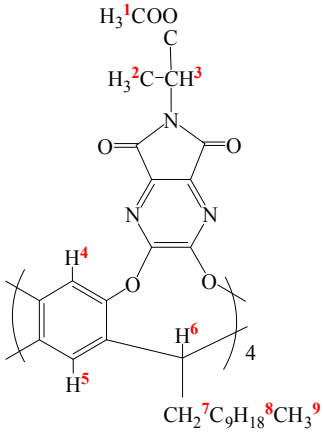
9. FTICR-MS of GUA (M=GUA).



10. Particle size comparison between GUE, GUNa, and GUA.

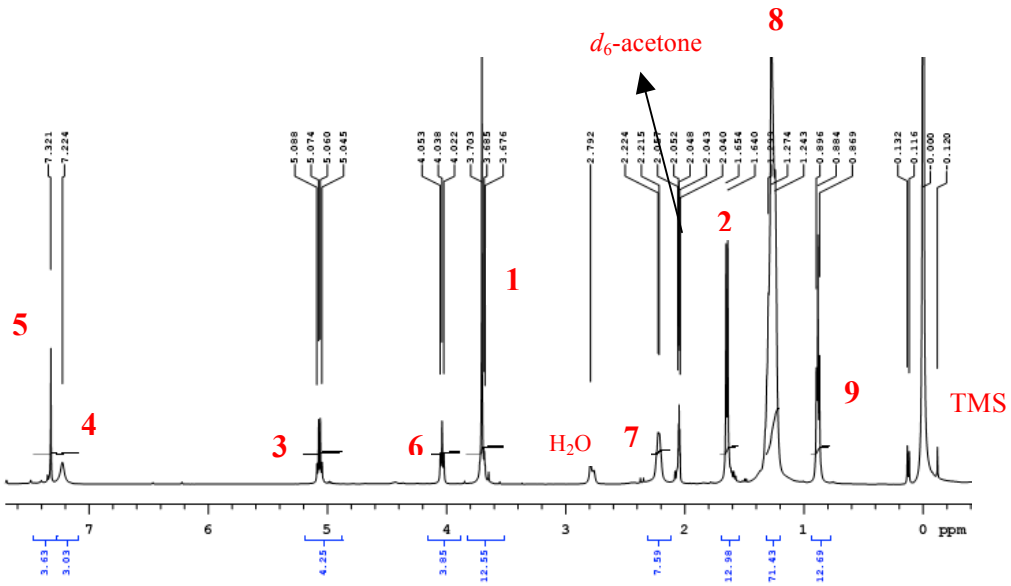


Characterization of AUE, AUNa, and AUA.

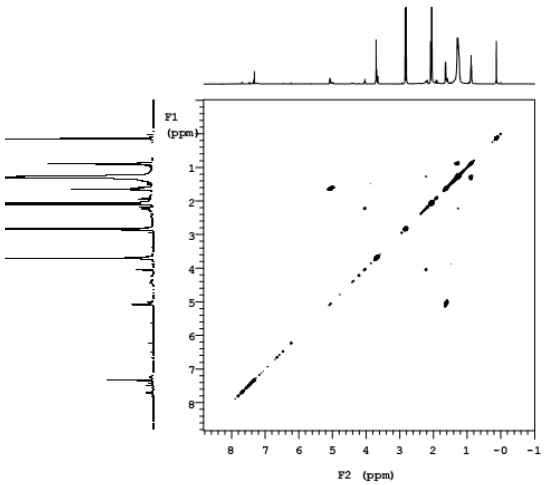


The structure of AUA

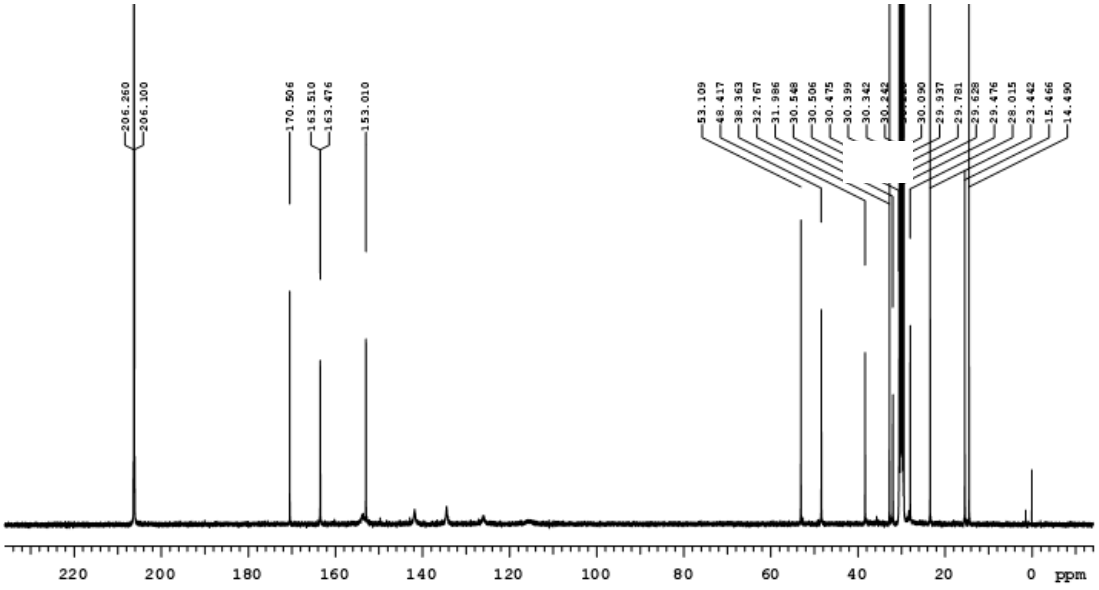
1. ^{1}H NMR of AUE in d_6-acetone.



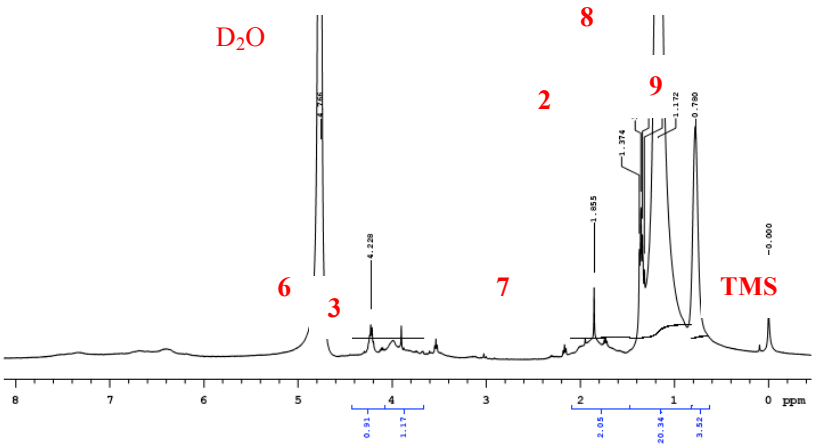
2. 2D COSY of AUE in d_6-acetone.



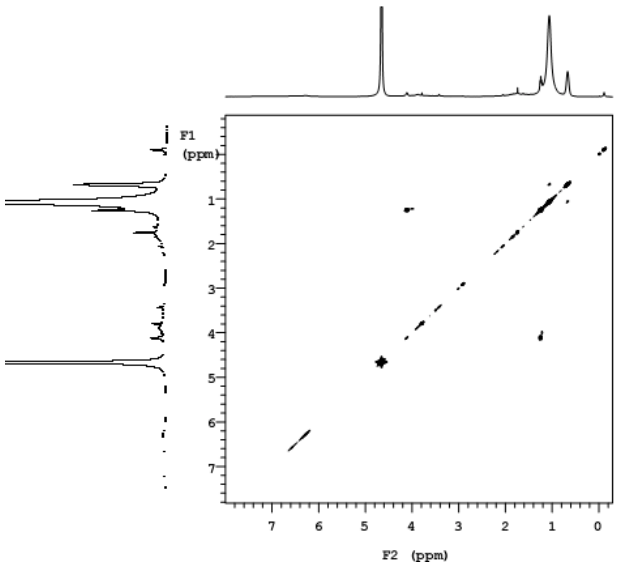
3. ^{13}C NMR of AUE in d_6-acetone.



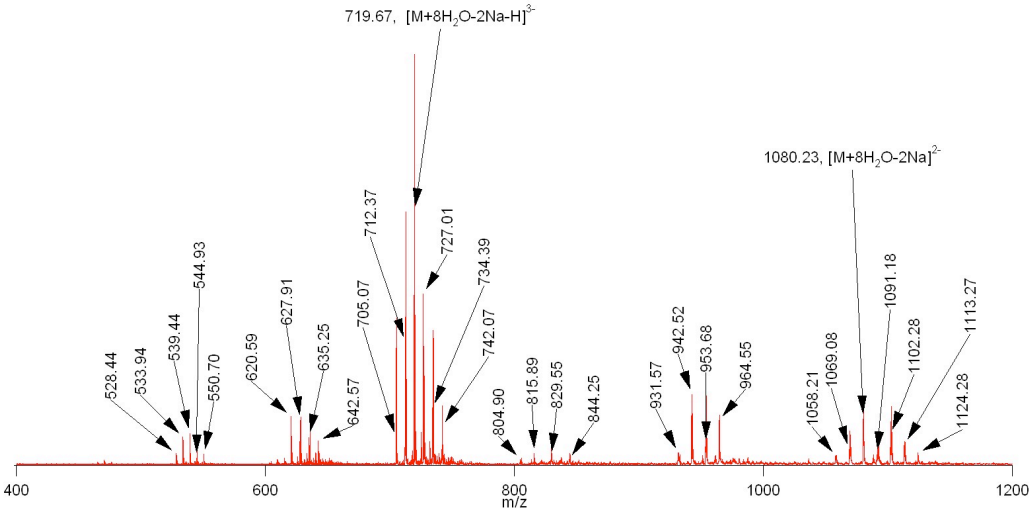
4. ^{1}H NMR of AUNa in D_2O.



5. 2D COSY AUNa in D_2O.

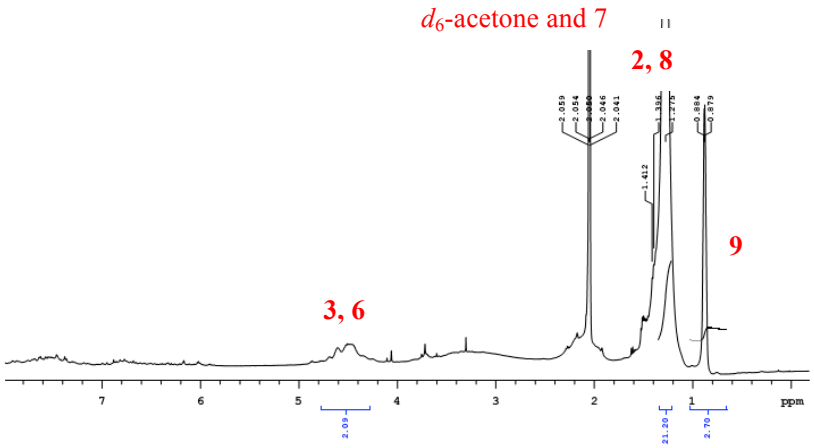


6. FTICR-MS of AUNa (M = AUNa).

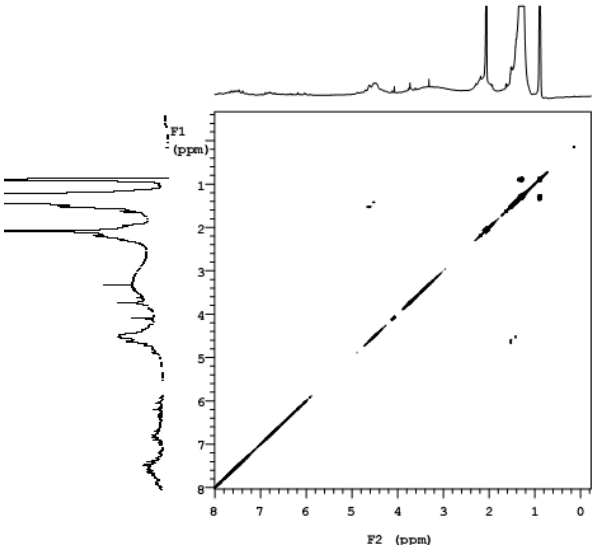


$[M+8H_2O-2Na-H]^{3-}$ = 719.67 (Calculated: 719.77); $[M+8H_2O-Na-2H]^{3-}$ = 727.01; $[M+8H_2O-3H]^{3-}$ = 743.39; $[M+8H_2O-3Na]^{3-}$ = 712.37; $[M+8H_2O-3Na]^{3-}$ = 712.37; $[M+8H_2O-4Na]^{4-}$ = 528.44; $[M+8H_2O-3Na-H]^{4-}$ = 533.94; $[M+8H_2O-2Na-2H]^{4-}$ = 539.44; $[M+8H_2O-1Na-3H]^{4-}$ = 544.93; $[M+8H_2O-4H]^{4-}$ = 550.70; $[M+8H_2O-2Na]^{2-}$ = 1080.23; $[M+8H_2O-Na-H]^{2-}$ = 1091.18; $[M+8H_2O-2H]^{2-}$ = 1102.28; $[M+8H_2O+Na-3H]^{2-}$ =113.27; $[M+8H_2O-2Na-1Arm]^{2-}$ = 942.52; $[M+8H_2O-Na-1Arm-H]^{2-}$ =953.68; $[M+8H_2O-2Na-2Arm]^{2-}$ = 804.90; $[M+8H_2O-Na-2Arm-H]^{2-}$ = 815.89; these peaks around 627.91 are the -3 peaks of -2 peaks around 942.52.

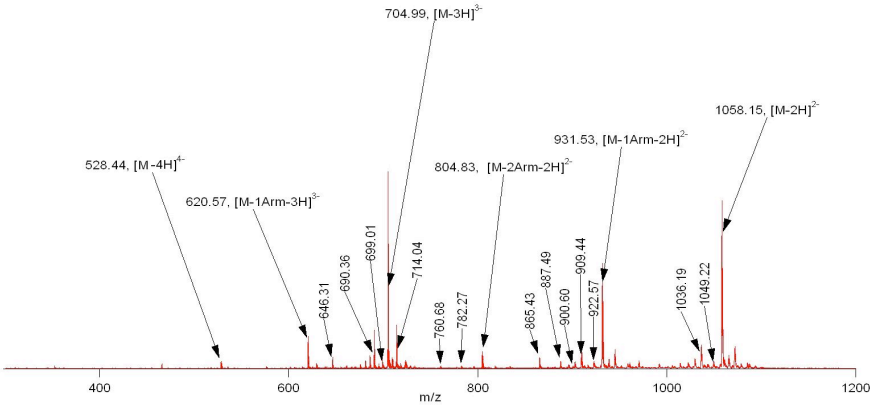
7. ^{1}H NMR of AUA in d_6-acetone.



8. 2D COSY of AUA in d_6-acetone.



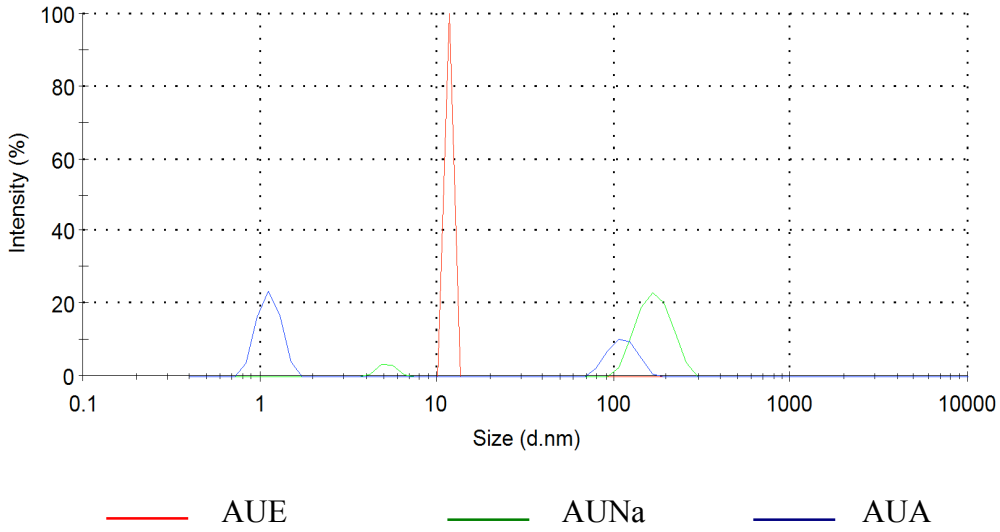
9. FTICR-MS of AUA (M = AUA+8H_2O).



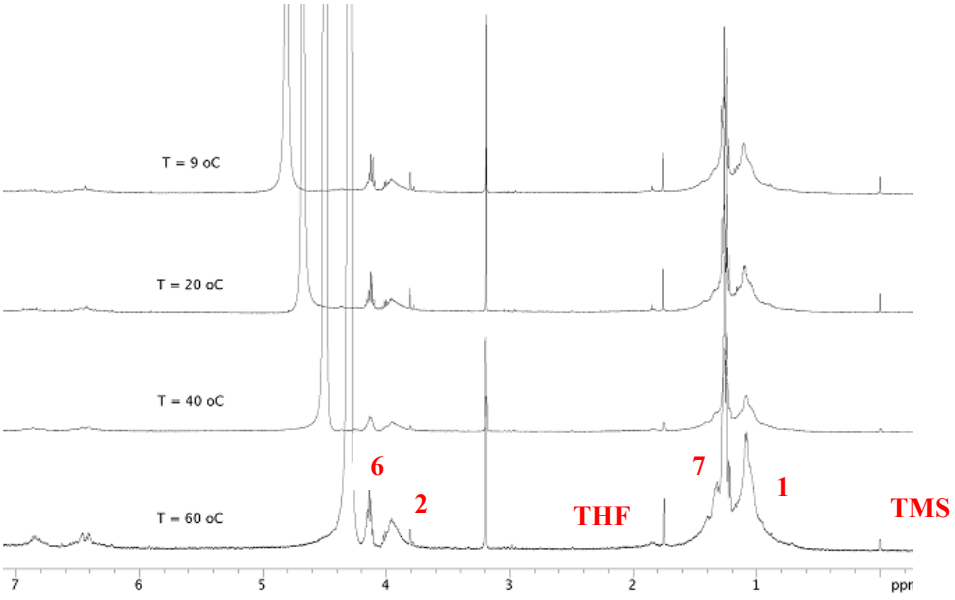
$[M-3H]^{3-}$ =704.99 (Calculated: 705.11). $[M-2H-H_2O]^{2-}$ = 1049.22; $[M-2H-CO_2]^{2-}$ = 1036.19; $[M-2H-1Arm-H_2O]^{2-}$ = 922.57; $[M-2H-1Arm-CO_2]^{2-}$ = 909.44; $[M-2H-1Arm-CO_2-H_2O]^{2-}$ = 900.60; $[M-2H-1Arm-2CO_2]^{2-}$ = 987.49; $[M-2H-1Arm-3CO_2]^{2-}$ = 965.43; $[M-2Arm-2H]^{2-}$ = 804.83; $[M-2Arm-2H-CO_2]^{2-}$ = 782.27; $[M-2Arm-2H-2CO_2]^{2-}$ = 760.68; $[M-3H-H_2O]^{3-}$ =699.01; $[M-3H-CO_2]^{3-}$ =690.36; $[M-3H-4CO_2]^{3-}$ =646.31; $[M-3H-1Arm]^{3-}$ =620.57; $[M-4H]^{4-}$ =528.44.

10. Particle size comparison between AUE, AUNa, and AUA.

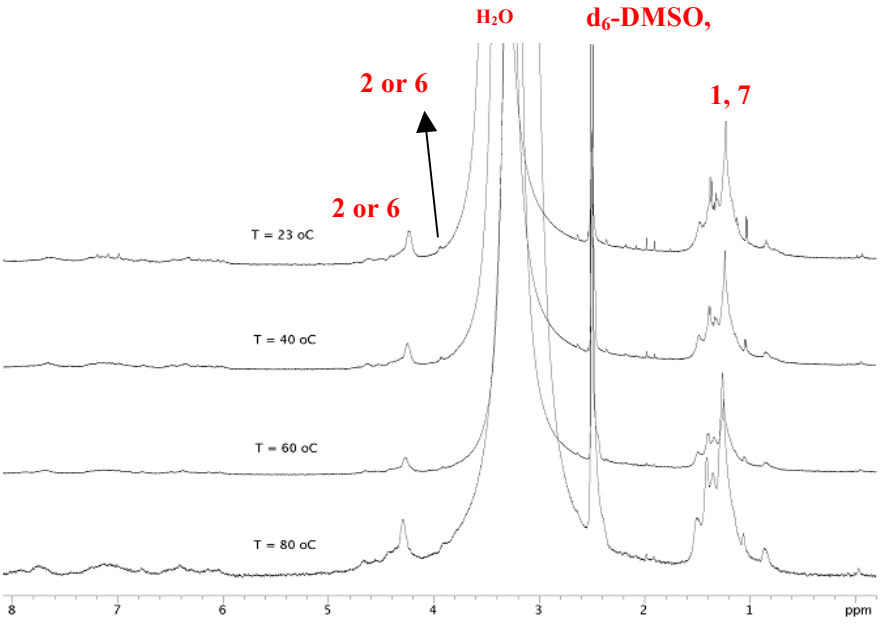
Size Distribution by Intensity



Various temperatures ^{1}H NMR study of AMNa in D_2O.



Various temperatures ^{1}H NMR study of AMA in d_6-DMSO.



Equilibrium Constant Calculations

To calculate equilibrium constants, we used a similar method to that previously published (J. S. Gardner, M. Conda-Sheridan, D. N. Smith, R. G. Harrison, J. D. Lamb, *Inorg. Chem.* 2005, **44**, 4295.). Briefly, we assume that the binding sites on AUA are independent of each other and thus, we can use a 1:1 binding isotherm of amine binding to AUA and equation 3, where H = AUA, G = amine, and HG = AUA-amine complex. There probably is some affect of the individual arms towards each others binding, but we treat this as negligible and thus we are able to calculate relative equilibrium constants.

$$H + G \rightleftharpoons HG \qquad K = \frac{[HG]}{[H][G]} \tag{3}$$

The observed chemical shift of amine guest can be expressed as:

$$\delta_{obs} = f_{10}\delta_G + f_{11}\delta_{HG} \tag{4}$$

where $f_{10} = \frac{[G]}{[G]+[HG]}$ is the fraction of free guest, δ_G is the chemical shift of free guest, $f_{11} = \frac{[HG]}{[G]+[HG]}$ is the fraction of host-guest complex, δ_{HG} is the chemical shift of host-guest complex. Since $f_{10} + f_{11} = 1$, equation 4 can be written

$$\delta_{obs} = (1- f_{11})\delta_G + f_{11}\delta_{HG} \tag{5}$$

Defining chemical shift difference $\Delta = \delta_{obs} - \delta_G$, $\Delta_{11} = \delta_{HG} - \delta_G$, and combing equation 5 with equation 3,

$$f_{11} = \frac{\Delta}{\Delta_{11}} = \frac{K[H]}{1 + K[H]} \tag{6}$$

Equation 6 can be written as:

$$\frac{\Delta}{[H]} = -K\Delta + \Delta_{11}K \qquad (7)$$

To put [H] in terms of total host concentration, we can use the mass balance equation:

$$[H_t] = [HG] + [H] = [H] + \frac{\Delta}{\Delta_{11}}[G_t] \qquad (8)$$

where $[H_t]$ is the total concentration of the guest.

Equation 7 can be written as :

$$\Delta = \frac{\Delta_{11}K([H_t] - \frac{\Delta}{\Delta_{11}}[G_t])}{1 + K([H_t] - \frac{\Delta}{\Delta_{11}}[G_t])} \qquad (9)$$

By preparing a plot of Δ vs $[H_t] - \frac{\Delta}{\Delta_{11}}[G_t]$ for each amine titration and performing a nonlinear fit of the titration data using equation (9), where K and Δ_{11} are unknown, we can determine K for each amine guest.

As the amount of amine increases, the NMR chemical shifts of the amines move back upfield to where they are when no **AUA** is present. We used the NMR titration data after the chemical shift of the amine had begun to return to where it was without host, the part of the titration where equilibrium exists. For primary and secondary amines, this was after two equivalents of amine and for tertiary amines this came after a quarter of an equivalent of amine. Thus, the equilibrium constants are relative to each other and represent the strength of amine association to **AUA**.

The equilibrium constants (log *K*) of AUA with amines in d_6-DMSO at 296 K are shown below:

Amine	log *K*	Amine	log *K*
1R	0.95	1S	0.97
2R	1.36	2S	0.84

3R	0.31	3S	0.35