Supporting information for "SOLUTION STRUCTURE OF ZINC-SEAMED *C*-ALKYLPYROGALLOL[4]ARENE DIMERIC NANOCAPSULES"

In this supporting information, small-angle neutron scattering (SANS) data and DOSY NMR data for zinc-seamed C-propylpyrogallol[4]arene (PgC_nZn) nanocapsules has been reported. SANS data has been reduced and fitted to elliptical, cylindrical, spherical and core-shell models. The quality of the fit and physical plausibility of the structural parameters was used to evaluate which structure was the most likely solution structure of the nanocapsules. The scattering length densities (SLDs) for the nanocapsules and solvent were calculated and the analyses were done on Igor software provided by NIST. The scattering data for PgC_3Zn were fitted globally wherein both 1% and 5% mass fraction scattering data sets were fitted simultaneously. In the global fits, the SLDs for PgC_3Zn nanocapsules and the solvent d_6-DMSO were held fixed at the calculated values and the structural parameters common to each data set were optimized to provide the best fit. Only the concentration was free to vary between the two PgC_3Zn data sets. Scattering curves for PgC_3Zn were fitted to a polydisperse (Schulz) sphere, cylinder, bimodal Schulz sphere, core-shell sphere and uniform ellipsoid models. The scattering data for PgC_3Zn fitted best to the Schulz sphere model indicating the presence of only one spherical assembly in solution. The core shell sphere model gives a poor fit; however, NMR shows guest encapsulation. This indicates two possibilities: (a) molecule is small and difficult to distinguish between a core-shell versus spherical geometry in DMSO (b): the population of dimeric capsules with pyridine guest inside is small.

SANS data and results:

Calculated scattering length densities (SLD):

Sample	Molecular formula	Density (g/ml)	wavelength (Å)	SLD ($Å^{-2}$)
PgC_3Zn hexamer	$C_{360}H_{408}O_{96}Zn_{24}$	1.3	6	1.56E-06
PgC_3Zn dimer	$C_{138}H_{174}O_{33}Zn_8$	1.3	6	1.37E-06
Pyridine (core)	C_5H_5N	0.9819	6	1.79E-06

Global fit to smeared uniform ellipsoid model
Data file: PgC_3Zn dimer in DMSO-d_6

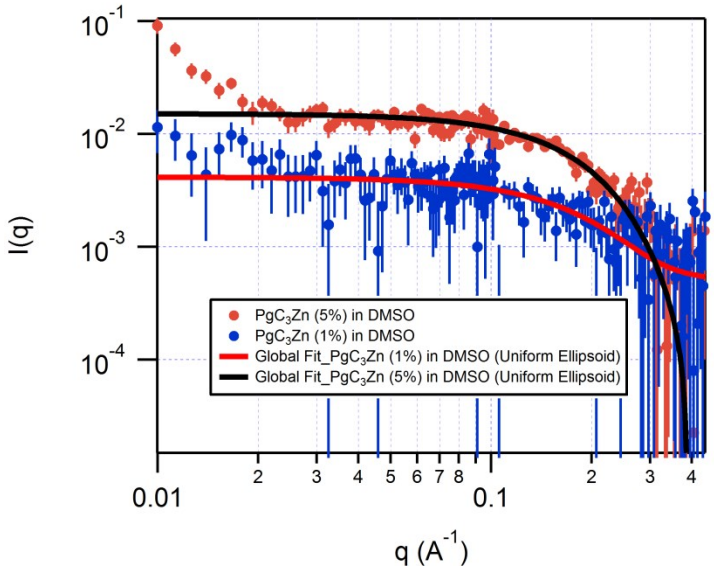

Figure S 1. Global fit for the zinc-seamed *C*-propylpyrogallol[4]arene dimer at mass fractions of 1% and 5%. The solid black line is the model fit with a smeared uniform ellipsoidal model. The error bars on the SANS data points represent one standard deviation in the measured intensity.

Global fit results Fit converged normally V_chisq = 466.737 V_npnts= 348 V_numNaNs= 0 V_numINFs= 0 Number of iterations: 2	
Data Set: PgC_3Zn_DMSO_1% ; Function: SmearedEllipsoidForm	
Volume fraction/scale	0.000493169 +- 0.000234842
Ra (rotation axis) (Å)	6.18702 +- 3.30953
Rb (Å)	13.7181 +- 0.801307
SLD ellipsoid ($Å^{-2}$)	1.37e-06 +- 0 *HELD
SLD solvent ($Å^{-2}$)	5.28e-06 +- 0 *HELD
Incoh. Bkg. (cm^{-1})	0.000491117 +- 0.000169971
Data Set: PgC_3Zn_DMSO_5% ; Function: SmearedEllipsoidForm	
Volume fraction/scale	0.0020925 +- 0.000989135
Ra (rotation axis) (Å)	6.18702 +- 3.30953 *LINKED to Pg3Zn_DMSO_1%; Ra (rotation axis)
Rb (Å)	13.7181 +- 0.801307 *LINKED to Pg3Zn_DMSO_1%; Rb
SLD ellipsoid ($Å^{-2}$)	1.37e-06 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; SLD ellipsoid
SLD solvent ($Å^{-2}$)	5.28e-06 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; SLD solvent
Incoh. Bkg. (cm^{-1})	-0.000400077 +- 0.000602692

Sqrt(χ^2/N) = 1.158, where N is the number of data points.
NOTE: The radius along the rotation axis of the ellipsoid has a large error bar for both PgC_3Zn 1% and 5% mass fraction samples and indicate a poor fit to the uniform ellipsoid model.

Global fit to smeared bimodal uniform ellipsoid model
Data file: PgC_3Zn dimer in DMSO-d_6

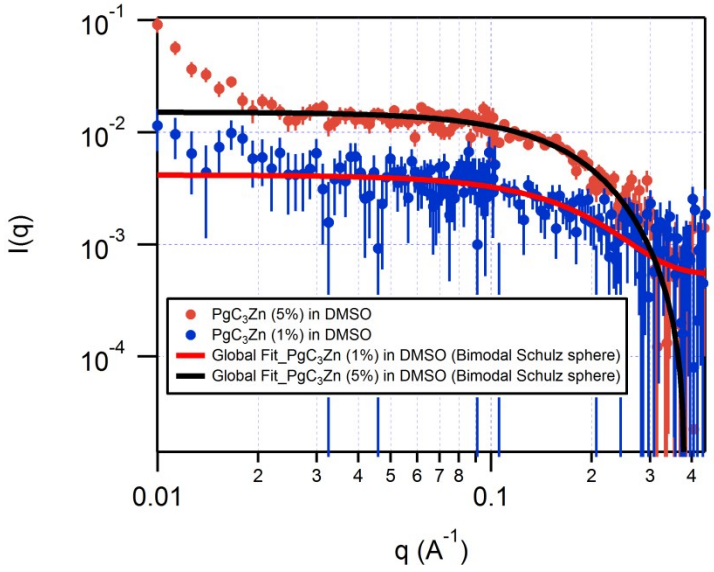

Figure S 2. Global fit for the zinc-seamed *C*-propylpyrogallol[4]arene dimer at mass fractions of 1% and 5%. The solid black line is the model fit with a smeared bimodal uniform ellipsoidal model. The error bars on the SANS data points represent one standard deviation in the measured intensity.

Global fit results		
Fit converged normally		
V_chisq = 465.727 V_npnts= 348 V_numNaNs= 0 V_numINFs= 0		
Number of iterations: 2		
Data Set: PgC_3Zn_DMSO_1% ; Function: SmearedBimodalSchulzSpheres		
Volume fraction 1	5.5891e-05 +- 1.29006	
Radius 1 (Å)	9.49086 +- 385.29	
Polydisp (sig/avg)	0.2 +- 0 *HELD	
SLD sphere1 (Å^{-2})	1.37e-06 +- 0	*HELD
Volume fraction 2	0.000416611 +- 1.42491	
Radius 2 (Å)	9.44889 +- 202.773	
Polydisp	0.2 +- 0 *HELD	
SLD sphere2 (Å^{-2})	1.56e-06 +- 0	*HELD
SLD solvent (Å^{-2})	5.28e-06 +- 0	*HELD
Incoh. Bkg. (cm^{-1})	0.000528864 +- 0.000252454	
Data Set: PgC_3Zn_DMSO_5% ; Function: SmearedBimodalSchulzSpheres		
Volume fraction 1	-0.00186442 +- 35.0313	
Radius 1 (Å)	9.49086 +- 385.29	*LINKED to Pg3Zn_DMSO_1%; Radius 1
Polydisp (sig/avg)	0.2 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; Polydisp	
SLD sphere1 (Å^{-2})	1.37e-06 +- 0	*HELD*LINKED to Pg3Zn_DMSO_1%; SLD sphere 1
Volume fraction 2	0.0041187 +- 38.7012	
Radius 2 (Å)	9.44889 +- 202.773	*LINKED to Pg3Zn_DMSO_1%; Radius 2
Polydisp(sig/avg)	0.2 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; Polydisp	
SLD sphere2 (Å^{-2})	1.56e-06 +- 0	*HELD*LINKED to Pg3Zn_DMSO_1%; SLD sphere 2
SLD solvent (Å^{-2})	5.28e-06 +- 0	*HELD*LINKED to Pg3Zn_DMSO_1%; SLD solvent
Incoh. Bkg. (cm^{-1})	-0.000269499 +- 0.000280926	

Sqrt(χ^2/N) = 1.157

NOTE: The negative volume fraction 2 reflects a poor fit to the bimodal Schulz sphere model and hence suggest the presence of only 1 species in solution.

Global fit to smeared cylinder model
Data file: PgC_3Zn dimer in DMSO-d_6

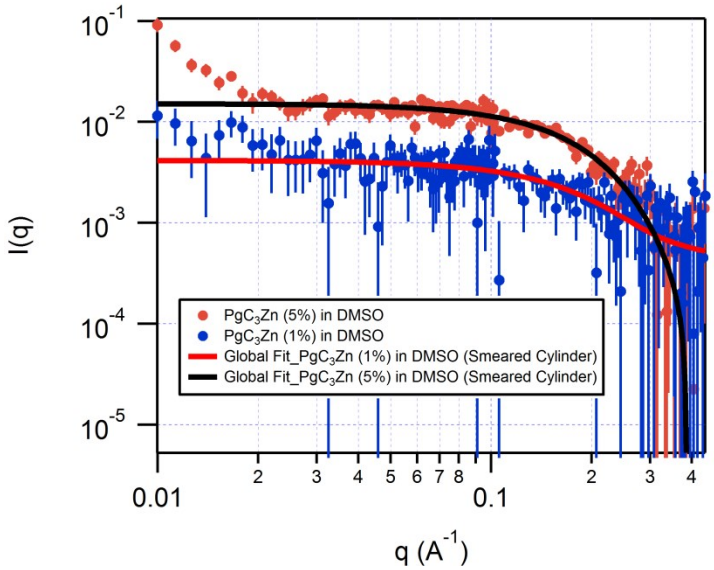

Figure S 3. Global fit for the zinc-seamed *C*-propylpyrogallol[4]arene dimer at mass fractions of 1% and 5%. The solid black line is the model fit with a smeared cylinder model. The error bars on the SANS data points represent one standard deviation in the measured intensity.

Global fit results	
Fit converged normally	
V_chisq = 466.5 V_npnts= 348 V_numNaNs= 0 V_numINFs= 0	
Number of iterations: 2	
Data Set: PgC_3Zn_DMSO_1%	; Function: SmearedCylinderForm
Scale	0.00225737 +- 0.520071
Radius (Å)	12.4615 +- 2.86151
Length (Å)	2.316 +- 529.756
SLD cylinder ($Å^{-2}$)	1.37e-06 +- 0 *HELD
SLD solvent ($Å^{-2}$)	5.28e-06 +- 0 *HELD
Incoh. Bkg. (cm^{-1})	0.000272369 +- 0.0082522
Data Set: PgC_3Zn_DMSO_5%	; Function: SmearedCylinderForm
Scale	0.00957513 +- 2.20599
Radius (Å)	12.4615 +- 2.86151 *LINKED to Pg3Zn_DMSO_1%; Radius
Length (Å)	2.316 +- 529.756 *LINKED to Pg3Zn_DMSO_1%; Length
SLD cylinder ($Å^{-2}$)	1.37e-06 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; SLD cylinder
SLD solvent ($Å^{-2}$)	5.28e-06 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; SLD solvent
Incoh. Bkg. (cm^{-1})	-0.0013264 +- 0.0350002

Sqrt(χ^2/N) = 1.158
NOTE: The negative volume fraction 2 reflects a poor fit to the bimodal Schulz sphere model and hence suggest the presence of only 1 species in solution.

Global fit to smeared core-shell sphere model
Data file: PgC_3Zn dimer in DMSO-d_6

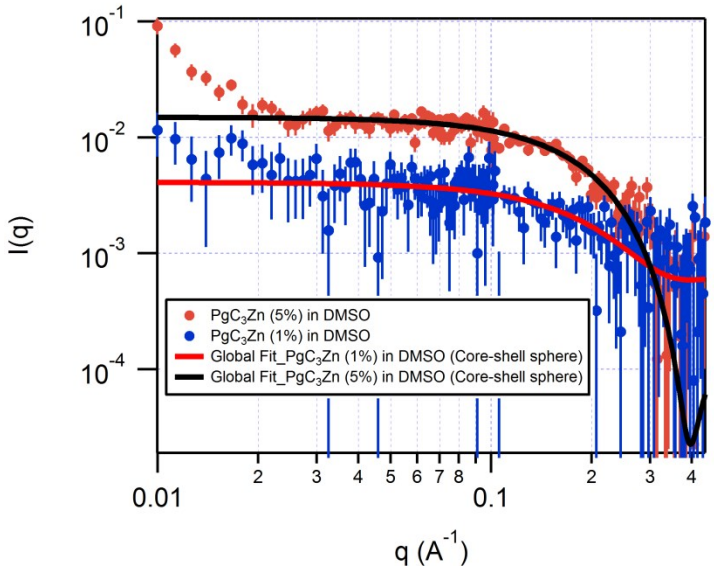

Figure S 4. Global fit for the zinc-seamed *C*-propylpyrogallol[4]arene dimer at mass fractions of 1% and 5%. The solid black line is the model fit with a smeared core shell sphere model. The error bars on the SANS data points represent one standard deviation in the measured intensity.

Global fit results	
Fit converged normally	
V_chisq = 474.911 V_npnts= 348 V_numNaNs= 0 V_numINFs= 0	
Number of iterations: 3	
Data Set: PgC_3Zn_DMSO_1%	; Function: SmearedCoreShellSphere
Scale	0.000440256 +- 0.000603636
Core radius (Å)	10.3387 +- 39.9205
Shell thickness (Å)	1.04545 +- 37.7551
Core SLD (Å^{-2})	1.79e-06 +- 0 *HELD
Shell SLD (Å^{-2})	1.37e-06 +- 0 *HELD
Solvent SLD (Å^{-2})	5.28e-06 +- 0 *HELD
Bkg (cm $^{-1}$)	0.000588743 +- 9.66268e-05
Data Set: PgC_3Zn_DMSO_5%	; Function: SmearedCoreShellSphere
Scale	0.00187109 +- 0.00256322
Core radius (Å)	10.3387 +- 39.9205 *LINKED to Pg3Zn_DMSO_1%; Core radius
Shell thickness (Å)	1.04545 +- 37.7551 *LINKED to Pg3Zn_DMSO_1%; Shell thickness
Core SLD (Å^{-2})	1.79e-06 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; Core SLD
Shell SLD (Å^{-2})	1.37e-06 +- 0 *HELD*LINKED to Pg3Zn_DMSO_1%; Shell SLD
Solvent SLD (Å^{-2})	5.28e-06 +- 0 *HELD**LINKED to Pg3Zn_DMSO_1%; Solvent SLD
Bkg (cm $^{-1}$)	6.16598e-06 +- 0.00015459

Sqrt(χ^2/N) = 1.168
NOTE: The SLD of core was fixed to that of guest pyridine while the shell was fixed to that of zinc framework. The error bars on core radius and shell thickness parameters reflects a poor fit to the core shell

sphere model. This indicates 2 possibilities: (a) molecule is small and difficult to demarcate into a core shell geometry in DMSO (b): the population of dimeric capsules with pyridine guest inside is small.

Global fit to smeared Schulz sphere model
Data file: PgC_3Zn dimer in DMSO-d_6

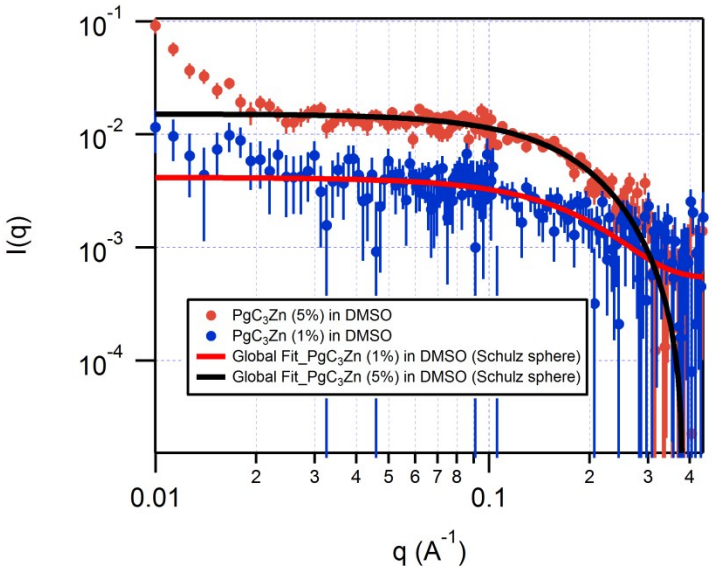

Figure S 5. Global fit for the zinc-seamed *C*-propylpyrogallol[4]arene dimer at mass fractions of 1% and 5%. The solid black line is the model fit with a smeared Schulz sphere model. The error bars on the SANS data points represent one standard deviation in the measured intensity.

Global fit parameters	
Fit stopped due to limit of iterations with no decrease in chi-square	
V_chisq = 465.738 V_npnts= 348 V_numNaNs= 0 V_numINFs= 0	
Number of iterations: 10	
Data Set: PgC_3Zn_DMSO_1%	; Function: SmearedSchulzSpheres
Volume fraction:	0.000439077 +- 3.58257e-05
Mean radius (Å)	9.40859 +- 0.182519
Polydisp (sig/avg)	0.2 +- 0 *HELD
SLD sphere ($Å^{-2}$)	1.37e-06 +- 0 *HELD
SLD solvent ($Å^{-2}$)	5.28e-06 +- 0 *HELD
Incoh. bkg. (cm^{-1})	0.00052209 +- 9.93389e-05
Data Set: PgC_3Zn_DMSO_5%	; Function: SmearedSchulzSpheres
Volume fraction:	0.00186264 +- 0.000108141
Mean radius (Å)	9.40859 +- 0.182519 *LINKED to Pg3Zn_DMSO_1%; radius
Polydisp (sig/avg)	0.2 +- 0 *HELD *LINKED to PgC3Zn_DMSO_1%; polydisp
SLD sphere ($Å^{-2}$)	1.37e-06 +- 0 *HELD*LINKED to PgC3Zn_DMSO_1%; SLD sphere
SLD solvent ($Å^{-2}$)	5.28e-06 +- 0 *HELD*LINKED to PgC3Zn_DMSO_1%; SLD solvent
Incoh. bkg. (cm^{-1})	-0.000268144 +- 0.000157842

Sqrt(χ^2/N) = 1.156
NOTE: The fit of the polydisperse spherical model reflects a a good fit and correlates well with a spherical shape of the nanocapsule.

NMR experimental section:

Capsules of [PgC_4Zn⊂(pyridine)] were synthesized by mixing methanolic solutions of *C*-butylpyrogallol[4]arene, zinc nitrate and pyridine in the ratio of 1:4:14. Sonication yielded precipitate of zinc dimers. A 2% solution of [PgC_4Zn⊂(pyridine)] was prepared in d_6-DMSO for NMR measurements. The ^1H and DOSY NMR were obtained on a Bruker Avance DRX500 spectrometer equipped with a 5mm cryogenically-cooled HCN triple resonance probe and a Z gradient coil. The operating frequency for ^1H was 500.13 MHz. All experiments were done at 25 °C. To minimize convection effect on DOSY measurement the sample was placed in a 3mm NMR tube. The Bruker supplied pulse sequence named "ledbpgp2s" was used with Z gradient strength stepping from 5 to 95% (total 16 data points). The probe's maximum Z gradient strength was 53.5 G/cm. The diffusion delay (d20) was set to 90 ms and the gradient pulse (p30) was set to 2.2 ms. Diffusion coefficient was obtained by fitting peak intensity as a function of gradient strength using Bruker supplied DOSY2D program.

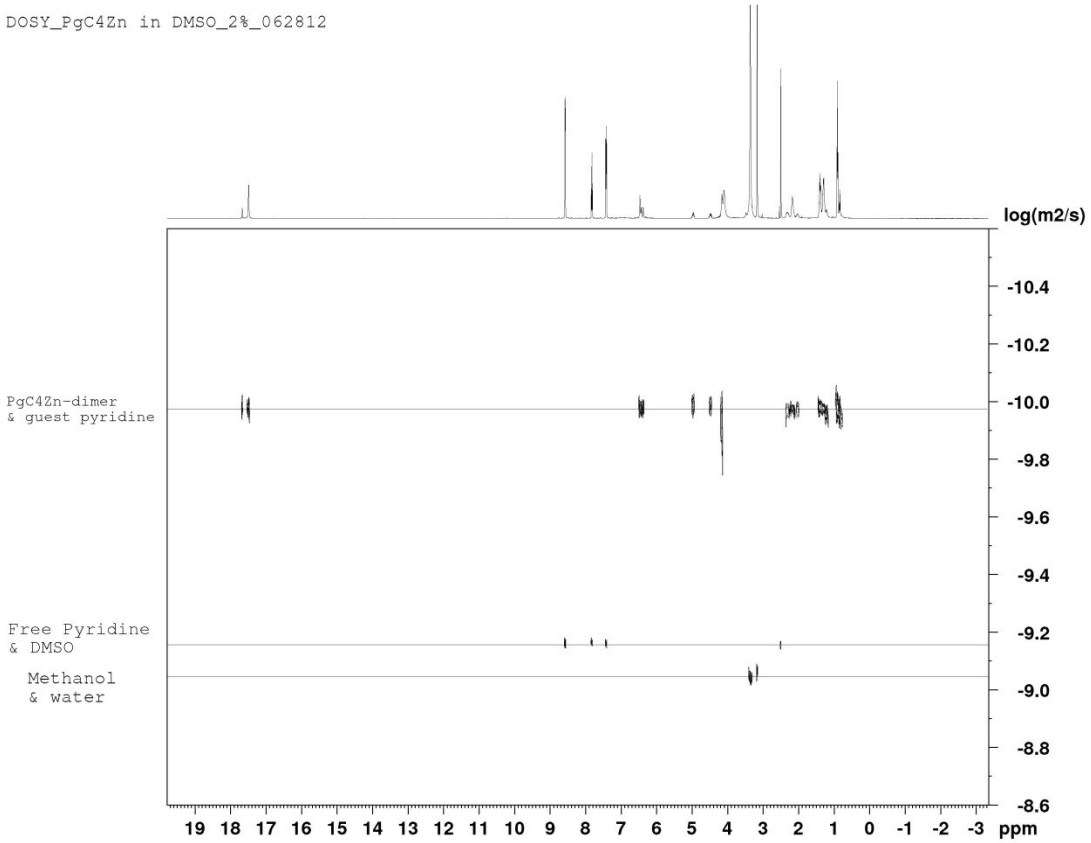

Figure S 6.The DOSY spectra of [$PgC_4Zn \subset$(pyridine)] dimer reveals a diffusion coefficient D of 1.04 $x10^{-10}$ m^2/sec for both the dimer host and the encapsulated guest molecule of pyridine. The diffusion coefficient of "free" pyridine ligand, solvent DMSO, methanol and water are 6.79 $x10^{-10}$, 7.00 $x10^{-10}$, 8.71 $x10^{-10}$ and 9.08 $x10^{-10}$ m^2/sec, respectively. Y-axis is displayed as logD.

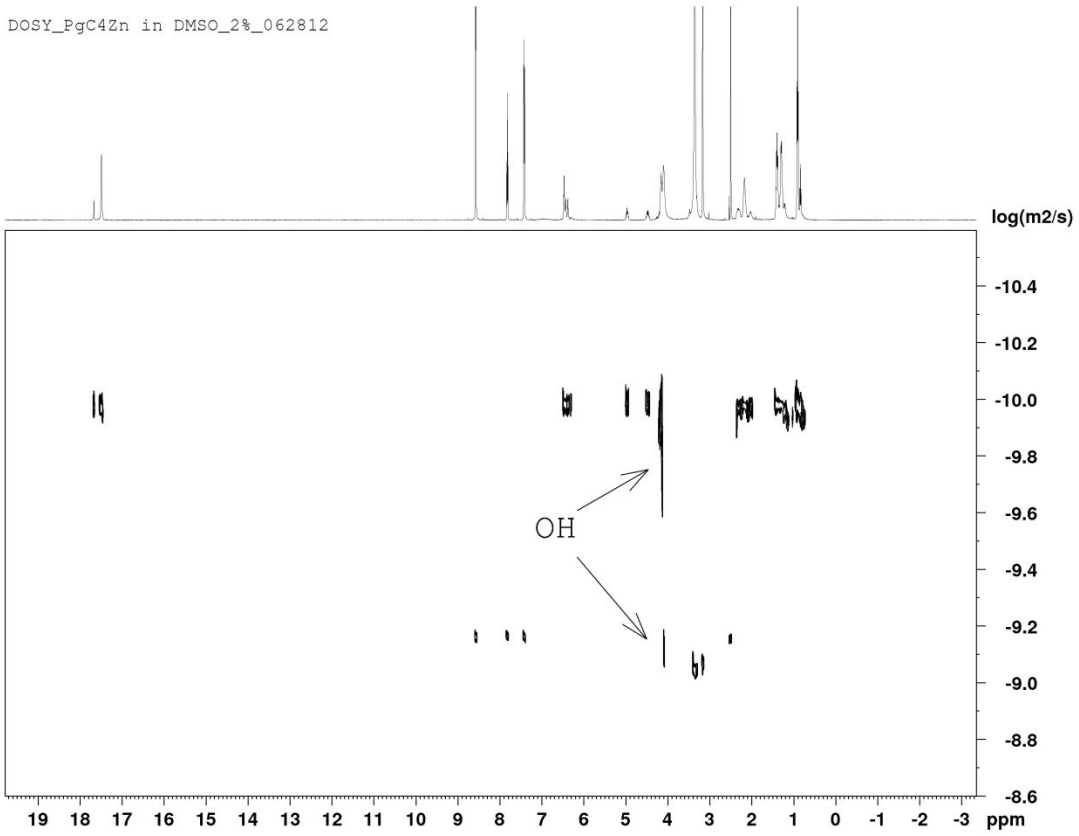

Figure S 7. The DOSY spectra of [PgC_4Zn⊂(pyridine)] dimer with magnified intensity scale reveals exchange between the methanol's OH signals between "bound" and "free" states. The "bound" state is when the OH is associated with the dimer and has an apparent D value close to that of the dimer. The"free" OH shows an apparent D close to that of DMSO. Due to the exchange averaging effect, the observed D values are not the true values when there is no exchange.