Supporting information (SANS, DLS, and UV) for

Aqueous solubilization of hydrophobic supramolecular metal-organic nanocapsules

In this supporting information, dynamic light scattering (DLS) data for zinc-seamed *C*-propylpyrogallol[4]arene (PgC_3Zn) dimer & PgC_3Cu hexamer and the small-angle neutron scattering (SANS) data for PgC_3Ni dimer, PgC_3Co dimer, PgC_3Cu hexamer (without external ligands) and PgC_3Ni hexamer (with external ligands) have been reported. (NOTE: The shortened formulae of nanocapsules are used throughout the *supporting information*, i.e. hexamers and dimers with actual chemical formula of $(PgC_3)_nM_{4n}L_{0-4n}$ are represented with PgC_3M hexamer/dimers with and without ligands.) The dimensions of micelles of aqueous-solubilized pyrogallol-based metal-seamed organic nanocapsules (MONCs) were studied on DLS and SANS to yield the hydrodynamic radius (R_h) and the static radius (R), respectively. Both R_h and R represent the size of the micelle; however, the R_h value for a given MONC is typically larger than R. R_h is the radius of a sphere that moves with a measured mobility, as defined in the Stokes-Einstein relation. Thus, DLS reports the radius of a sphere or R_h that accounts for the viscosity drag at the surface. The fit to the SANS data as polydisperse core-shell spheres, also reports a radius; however the SANS fit is a "static" fit, that is a snapshot (time-averaged) of the size of scatterers. For the reason of viscous drag, the R_h value is usually a little bit larger than the R found from a static measurement.

SANS data was reduced and fitted to elliptical, cylindrical, spherical and polydisperse core-shell hard sphere 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. For the Schulz sphere model, the SLDs for $PgC_3Zn/Cu/Ni/Co$ nanocapsules and the solvent D_2O were held fixed at the calculated values and the structural parameters common to each data set were optimized to provide the best fit. For the polydisperse core-shell hard sphere model the SLD of the core was

fixed to that of one nanocapsule plus approximately 50 surfactant molecules, and the shell thickness was free to fit, starting with an initial guess with a mixture of surfactant and D_2O. Solvent SLD was always fixed to the SLD of D_2O. The data for the micelles of surfactant/hexamers and surfactant/dimers fitted best to the polydisperse core-shell hard sphere model indicating the presence of spherical nanoassemblies in solution.

NOTE: The DLS results are summarized below. The low polydispersity and higher intensity signals indicate the monodisperse nature of micelles in aqueous solution. For the tween-60 micellar conditions the dilutions were extremely high resulting in low intensity and poor reproducibility and thus cannot be considered as reliable results. Tween 20/span 80 and tween 80/span 80 have low intensity as well, and thus poor statistics.

	0.4 m^3/ m^3	Radius (nm)	Polyd	Intensity
1	Tween-20	3.66	24.2	94.4
		3.87	27.6	90.6
	Avg	3.77	25.9	92.5
2	Tween-40	3.97	12.50	100
		4.11	19.8	100
	Avg	4.04	16.15	100
4	Tween-80	3.82	15.7	94.8
		3.67	18.2	93.7
	Avg	3.74	16.95	94.25
	0.6 m^3/ m^3	Radius (nm)	Polyd	Intensity
1	Tween-20	3.93	20.0	96.7
		3.65	18.2	97.8
		3.92	23.5	95.8
	Avg	3.83	20.57	96.77
2	Tween-40	4.07	9.30	94.2
		4.28	20.9	95.4
		4.14	6.20	91.0
	Avg	4.16	12.13	93.53
4	Tween-80	3.61	10.1	84.2
		3.69	17.8	89.2
		3.59	18.9	86.4
	Avg	3.63	15.6	86.6

Table 1. DLS data for *C*-propylpyrogallol[4]arene zinc dimer

	0.6 m^3/ m^3	Radius (nm)	Polyd	Intensity
1	Tween-20	4.22	22.7	88.5
		4.02	11.1	81.3
		4.47	15.9	82.3
	Avg	4.24	16.6	84.0
2	Tween-40	4.39	13.9	97.5
		4.44	12.6	91.9
		4.48	15.9	96.4
	Avg	4.44	14.1	95.3
4	Tween-80	3.67	18	84
		3.89	16.1	85.8
		3.80	16.1	87.0
	Avg	3.79	16.7	85.6
	0.4 m^3/ m^3	Radius (nm)	Polyd	Intensity
1	Tween-20	3.68	22.8	85.1
		3.41	21.6	82.2
		3.94	13.3	81.9
	Avg	3.68	19.2	83.1
2	Tween-40	4.01	11.5	84.6
		3.98	12.4	80.8
		4.03	10.6	85.3
		4.19	0	90.5
	Avg	4.05	8.6	85.3
4	Tween-80	3.70	17.7	85.9
		3.77	16.7	84.1
		3.86	19.2	85.2
	Avg	3.77	17.9	85.1

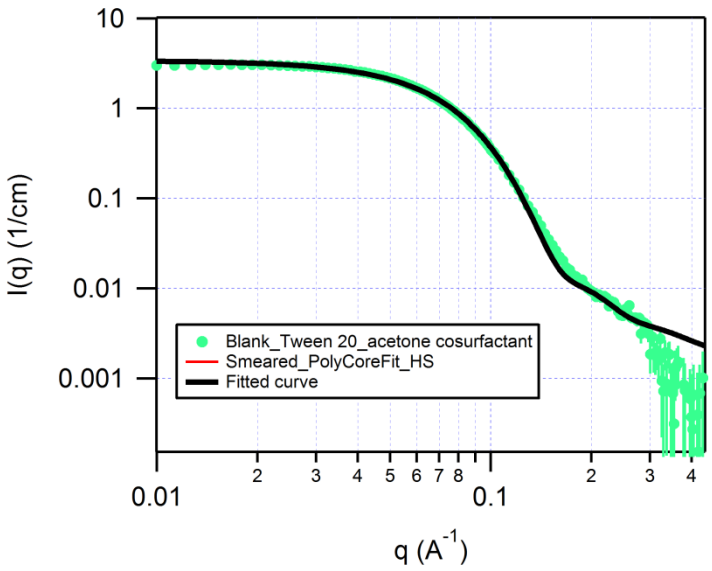
Table 2. DLS data for *C*-propylpyrogallol[4]arene copper hexamer

SANS RESULT SUMMARY AND DATA FITS:

S.No.	Sample	cosurfactant	Core Radius (Å)	Shell thickness (Å)	Chi-sqrt
1	Tween 20 (control)	acetone	12.04	16.35	6.23
2	Tween 20 (control)	acetonitrile	12.29	16.01	6.54
3	Tween 20 (control)	isopropanol	12.06	16.11	5.83
4	PgC_3Co dimer + Tween 20	isopropanol	17.04	16.62	1.51
5	PgC_3Ni hexamer + Tween 20	acetonitrile	24.66	12.95	2.48
6	Tween 80 (control)	DMSO	15.42	19.88	9.15
7	PgC_3Cu hexamer (without ligands) + Tween 80	None	24.09	17.26	2.60
8	PgC_3Ni dimer + Tween 80	DMSO	19.37	17.00	3.65
9	PgC_3Ni hexamer (with ligand) + Tween 80	DMSO	29.0218	16.54	5.53

Table 4. SANS Results Summary of Polydisperse Core-Shell Hard Sphere fits

Fit to Smeared Poly Core HS (Hard Sphere) model
Data file: Blank_D2O with Tween_20 surfactant/ acetone cosurfactant

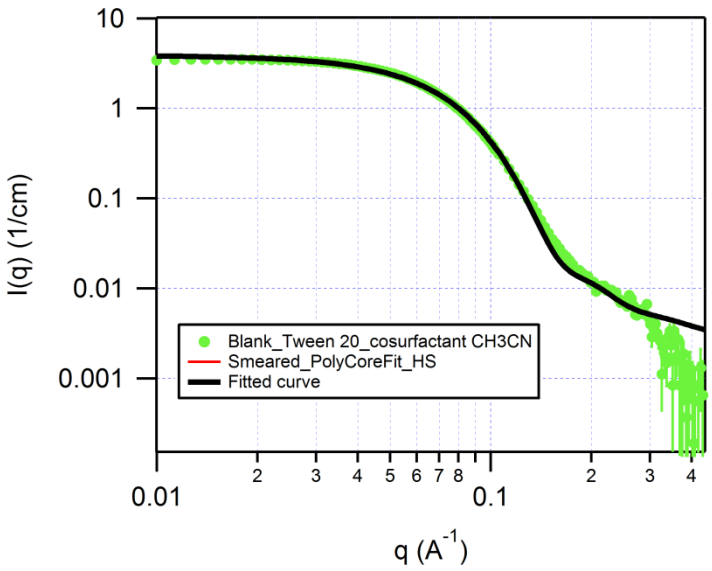


Volume fraction	0.0194143	±	0.000539073
Avg. core radius (Å)	12.0423	±	0.269235
core polydisp (0,1)	0.4	±	0.0098749
Shell thickness (Å)	16.3473	±	0.233687
SLD core ($Å^{-2}$)	5.94e-07	±	0
SLD shell ($Å^{-2}$)	2.28053e-06	±	4.33476e-08
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	0.00172365	±	0.000112919

chisq = 6846.92
Npnts = 174 **Sqrt(χ^2/N) = 6.27297**
Fitted range = [0,173] = 0.009974 < Q < 0.4385

NOTE: The average core radius of tween 20 surfactant/acetone cosurfactant micelles in D_2O is around 12 Å and the shell thickness is about 16 Å. The error bars on all parameters are low but the chi-sqrt value of 6 is little high, indicative of micelle surface roughness. Overall it gives a good approximation of micelle size. Note that the size of control sample micelles is unaffected by the presence of various cosurfactants/cosolvents (see other fits of control sample).

Fit to Smeared Poly Core HS (Hard Sphere) model
Data file: Blank_D2O with Tween 20 surfactant/ acetonitrile cosurfactant

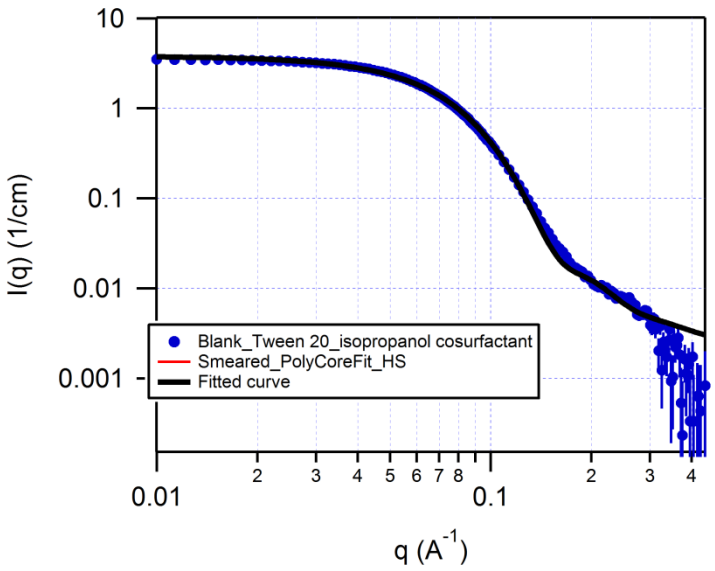


Volume fraction	0.0215987	±	0.000517061
Avg. core radius (Å)	12.2856	±	0.239013
core polydisp (0,1)	0.4	±	0.00864722
Shell thickness (Å)	16.0086	±	0.20758
SLD core ($Å^{-2}$)	5.94e-07	±	0
SLD shell ($Å^{-2}$)	2.21137e-06	±	4.04131e-08
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	0.00280876	±	0.000117302

chisq = 7439.52
Npnts = 174 **Sqrt(χ ^2/N) = 6.5388**
Fitted range = [0,173] = 0.009974 < Q < 0.4386

NOTE: The average core radius of tween 20 surfactant/acetonitrile cosurfactant micelles in D_2O is around 12 Å and the shell thickness is about 16 Å. The error bars on all parameters are low but the chi-sqrt value of 6.5 is little high, indicative of micelle surface roughness. Overall it gives a good approximation of micelle size. Note that the size of control sample micelles is unaffected by the presence of various cosurfactants/cosolvents (see other fits of control sample).

Fit to Smeared Poly Core HS (Hard Sphere) model
Data file: Blank_D2O with Tween 20 surfactant/ isopropanol cosurfactant



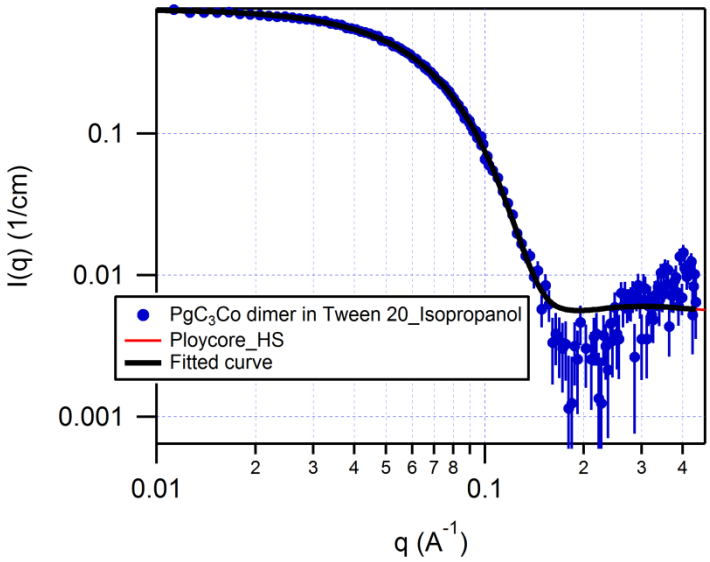
Volume fraction	0.0190125	±	0.000513148
Avg. core radius (Å)	12.0568	±	0.295253
core polydisp (0,1)	0.4	±	0.0103468
Shell thickness (Å)	16.1058	±	0.270098
SLD core ($Å^{-2}$)	5.94e-07	±	0
SLD shell ($Å^{-2}$)	1.87864e-06	±	4.42252e-08
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	0.00240368	±	0.000118829

chisq = 5916.3
Npnts = 174 **Sqrt(χ ^2/N) = 5.8311**
Fitted range = [0,173] = 0.009974 < Q < 0.4385

NOTE: The average core radius of tween 20 surfactant/isopropanl cosurfactant micelles in D_2O is around 12 Å and the shell thickness is about 16 Å. The error bars on all parameters are low but the chi-sqrt value of 6 is little high, indicative of micelle surface roughness. Overall it gives a good approximation of micelle size. Note that the size of control sample micelles is unaffected by the presence of various cosurfactants/cosolvents (see other fits of control sample).

Fit to Smeared Poly Core HS (Hard Sphere) model

Data File: PgC_3Co dimer in D2O with Tween 20 surfactant/ isopropanol cosurfactant



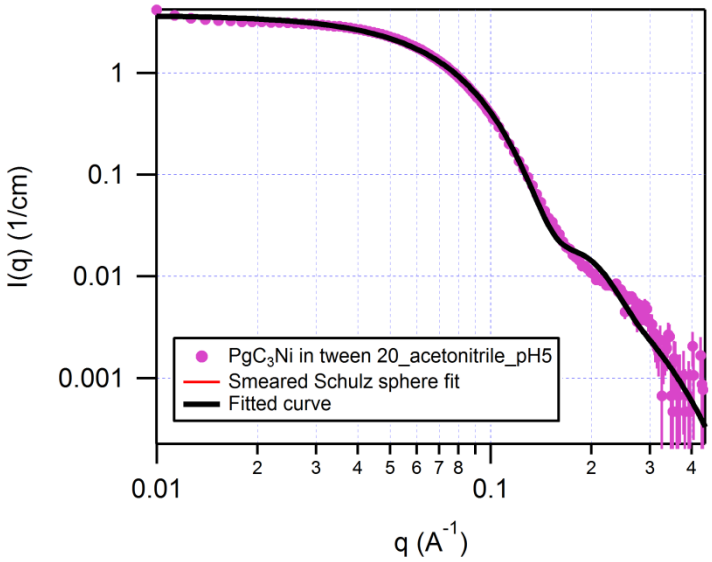
Volume fraction	0.00732613	±	0.0016239
Avg. core radius (Å)	17.0362	±	2.23863
core polydisp (0,1)	0.232474	±	0.0516247
Shell thickness (Å)	16.6191	±	1.20221
SLD core ($Å^{-2}$)	6.53e-07	±	0
SLD shell ($Å^{-2}$)	4.74694e-06	±	3.37988e-07
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	0.00561796	±	0.000213238

chisq = 396.234
Npnts = 174 **Sqrt(χ^2/N) = 1.50904**
Fitted range = [0,173] = 0.009974 < Q < 0.4385

NOTE: The average core radius of tween 20⊂PgC_3Co dimeric micelles is around 17 Å and the shell thickness is about 16.6 Å. The error bars on all parameters are low and the chi-sqrt value of 1.5 is low, indicative of good statistics and uniformity of micelles. Overall it gives a good approximation of dimer enclosed micelle size. Note that the avg. core radius size of tween 20⊂PgC_3Co dimeric micelles (17 Å) is larger than that of control (tween 20 in D_2O).

Fit to Smeared Poly Core HS (Hard Sphere) model

Data file: PgC_3Ni hexamer in D2O with Tween 20 surfactant/ d3-acetonitrile cosurfactant



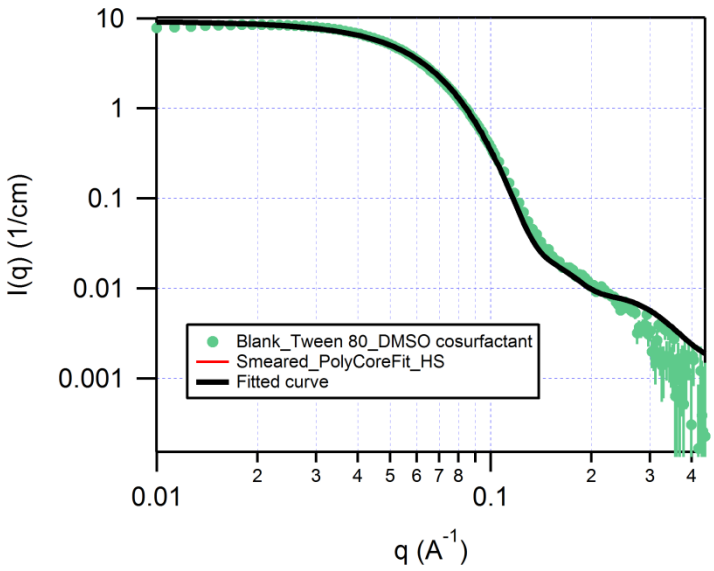
Volume fraction	0.0312979	±	0.000366214
Avg. core radius (Å)	24.6612	±	0.142746
core polydisp (0,1)	0.240584	±	0.0020484
Shell thickness (Å)	12.9475	±	0.10611
SLD core ($Å^{-2}$)	6.59e-07	±	0
SLD shell ($Å^{-2}$)	6.32271e-06	±	2.15244e-08
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	0.000397313	±	0.000116663

chisq = 1066.92
Npnts = 174 **Sqrt(χ^2/N) = 2.47623**
Fitted range = [0,173] = 0.009974 < Q < 0.4385

NOTE: The average core radius of tween 20⊂PgC_3Ni hexameric micelles is around 24 Å and the shell thickness is about 13 Å. The error bars on all parameters are low and the chi-sqrt value of 2.5 is low, indicative of good statistics and uniformity of micelles. Overall it gives a good approximation of hexamer enclosed micelle size. Note that the avg. core radius size of tween 20⊂PgC_3Ni hexameric micelles (24 Å) is larger than that of tween 20⊂PgC_3Co dimeric micelles (17 Å) and control (tween 20 in D_2O; 12 Å) samples.

Fit to Smeared Poly Core HS (Hard Sphere) model

Data file: Blank_D2O with Tween 80 surfactant/ d6-DMSO cosurfactant



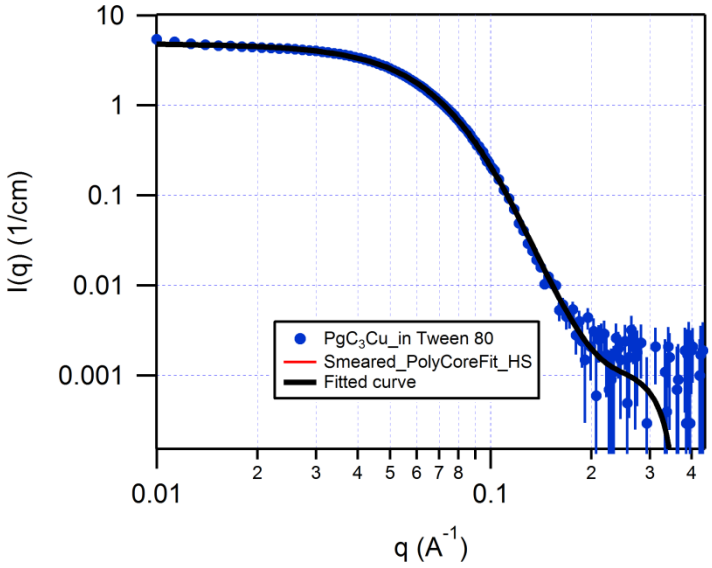
Volume fraction	0.041305	±	0.00040501
Avg. core radius (Å)	15.4222	±	0.098369
core polydisp (0,1)	0.39	±	0.00363903
Shell thickness (Å)	19.8868	±	0.0717118
SLD core ($Å^{-2}$)	5.57e-07	±	0
SLD shell ($Å^{-2}$)	2.94299e-06	±	1.58254e-08
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	0.00147511	±	0.000105904

chisq = 14570.9
Npnts = 174 **Sqrt(χ^2/N) = 9.151**
Fitted range = [0,173] = 0.009974 < Q < 0.4385

NOTE: The average core radius of tween 80 surfactant/DMSO cosurfactant micelles in D_2O is around 15 Å and the shell thickness is about 19 Å. The error bars on all parameters are low but the chi-sqrt value of 9 is little high, indicative of micelle surface roughness. Overall it gives a good approximation of micelle size.

Fit to Smeared Poly Core HS (Hard Sphere) model

Data file: PgC_3Cu hexamer in D2O with Tween 80 surfactant



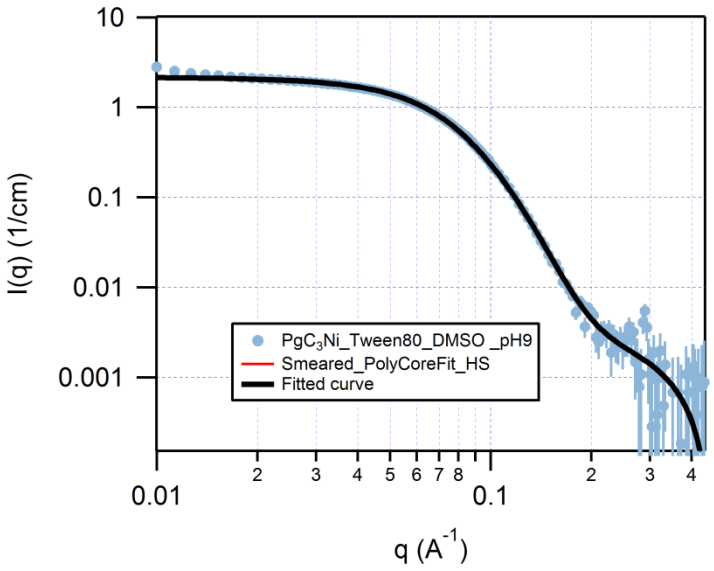
Volume fraction	0.0330463	±	0.000997167
Avg. core radius (Å)	24.0962	±	0.549751
core polydisp (0,1)	0.283912	±	0.00999678
Shell thickness (Å)	17.2643	±	0.156072
SLD core ($Å^{-2}$)	6.9e-07	±	0
SLD shell ($Å^{-2}$)	5.6179e-06	±	4.18476e-08
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	-0.00122171	±	0.000168092

chisq = 1176.39
Npnts = 174 **Sqrt(χ^2/N) = 2.60017**
Fitted range = [0,173] = 0.009974 < Q < 0.4385

NOTE: The average core radius of tween 80⊂PgC_3Cu hexameric (no external ligands) micelles is around 24 Å and the shell thickness is about 17 Å. The error bars on all parameters are low and the chi-sqrt value of 2.6 is small, indicative of good statistics and uniformity of micelles. Overall it gives a good approximation of hexamer enclosed micelle size.

Fit to Smeared Poly Core HS (Hard Sphere) model

Data File: PgC_3Ni dimer in D2O with Tween 80 surfactant



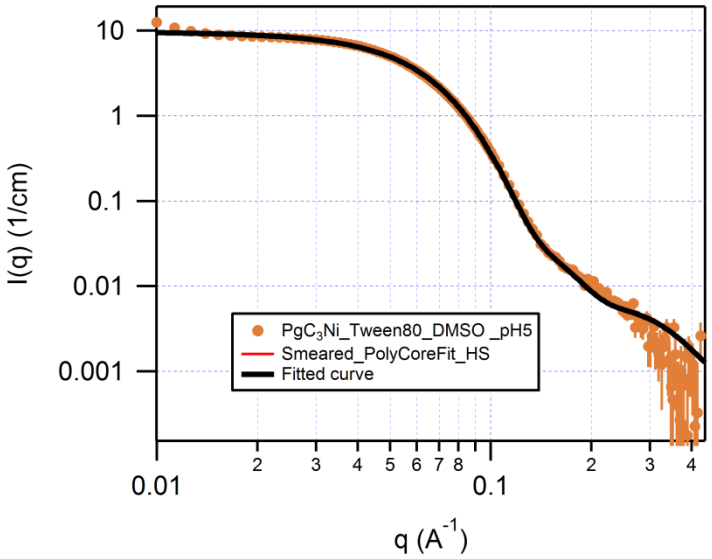
Volume fraction	0.0346267	±	0.00203674
Avg. core radius (Å)	19.376	±	0.948869
core polydisp (0,1)	0.320975	±	0.022902
Shell thickness (Å)	17	±	0.0978275
SLD core ($Å^{-2}$)	6.6e-07	±	0
SLD shell ($Å^{-2}$)	5.96101e-06	±	5.95204e-08
SLD solvent ($Å^{-2}$)	6.62e-06	±	0
bkg (cm^{-1})	-0.000369782	±	0.000134225

chisq = 2321.27
Npnts = 174 **Sqrt(χ^2/N) = 3.65249**
Fitted range = [0,173] = 0.009974 < Q < 0.4385

NOTE: The average core radius of tween 80⊂PgC_3Ni dimeric micelles is around 19 Å and the shell thickness is about 17 Å. The error bars on all parameters are low but the chi-sqrt value of 3.6 is little high, indicative of micelle surface roughness. Overall it gives a good approximation of dimer enclosed micelle size.

Fit to Smeared Poly Core HS (Hard Sphere) model

Data file: PgC_3Ni hexamer (with ligands) in D_2O with Tween 80 surfactant/ DMSO cosurfactant



Volume fraction	0.0507419	±	0.000287104
Avg. core radius (Å)	29.0218	±	0.0968636
core polydisp (0,1)	0.224085	±	0.00158368
Shell thickness (Å)	16.5438	±	0.0523239
SLD core ($Å^{-2}$)	6e-07	±	0
SLD shell ($Å^{-2}$)	5.9026e-06	±	9.91788e-09
SLD solvent ($Å^{-2}$)	6.6e-06	±	0
bkg (cm^{-1})	0.0790461	±	0.000100536

chisq = 5336.51

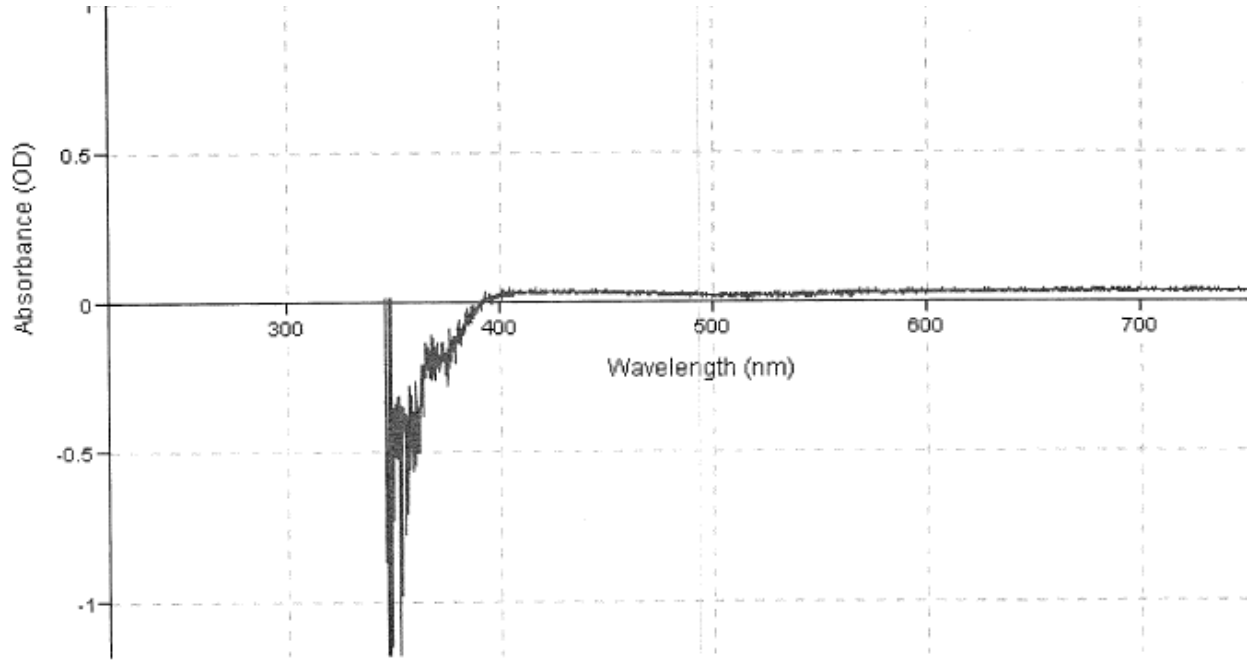
Npnts = 174 **Sqrt(χ^2/N) = 5.53801**

Fitted range = [0,173] = 0.009974 < Q < 0.4385

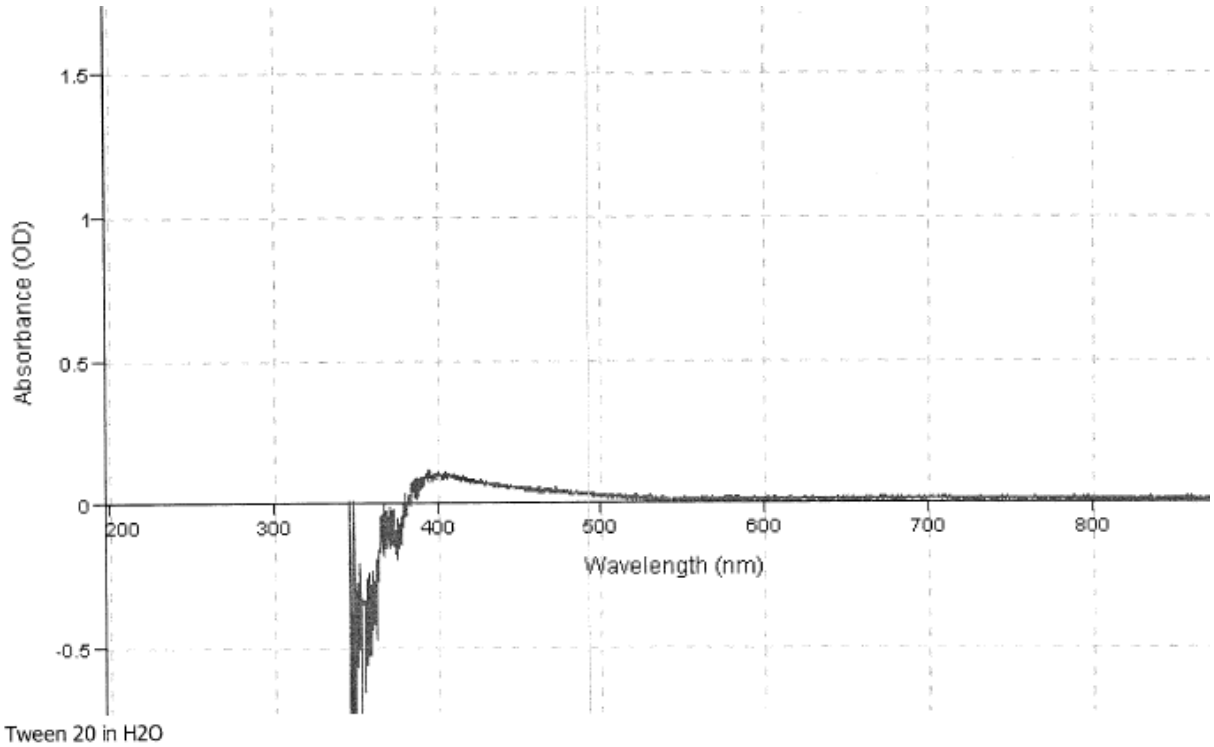
NOTE: The average core radius of tween 80⊂PgC_3Ni hexameric micelles is around 39 Å and the shell thickness is about 16.5 Å. The error bars on all parameters are low but the chi-sqrt value of 5.5 is little high, indicative of micelle surface roughness. Overall it gives a good approximation of hexamer enclosed micelle size. Note that the size of tween 80⊂PgC_3Ni hexameric micelles is larger than that of tween 80⊂PgC_3Ni dimer and tween 80⊂PgC_3Cu hexamer due to the presence of external ligands on the PgC_3Ni hexamer.

UV Spectrum

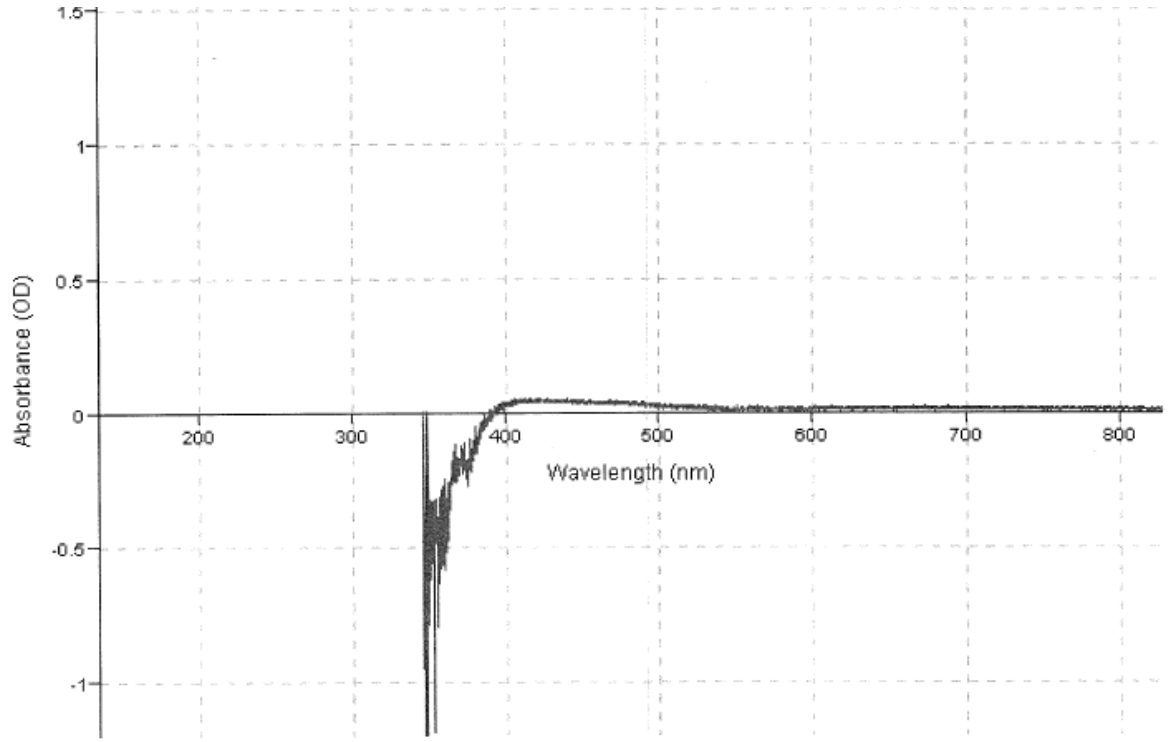
The UV spectra presented here give direct evidence of the solubilization of the nanocapsules within the micelles. There is little or no UV absorbance from the tweens or from the nanocapsules in water alone, while there is significant UV absorption when the nanocapsules are present with the tween micelles. Thus there is direct evidence that the micelles are solubilizing the colored nanocapsules. These measurements are qualitative, to show proof of solubilization.



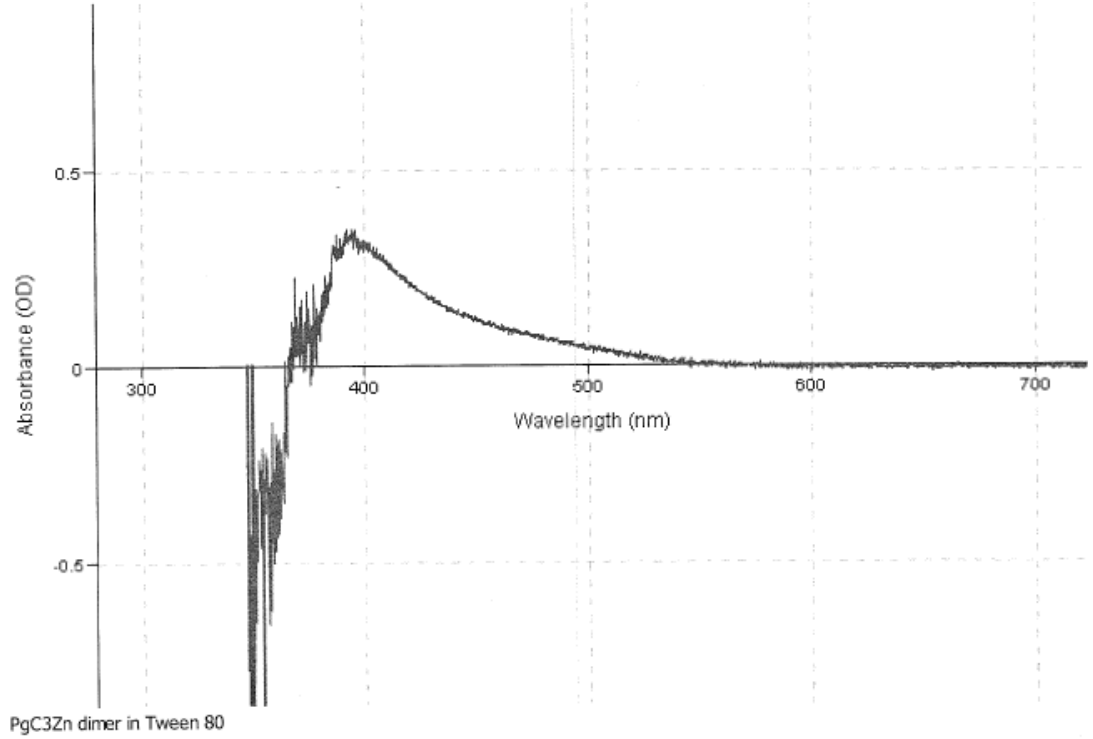
Tween 80 in D2O



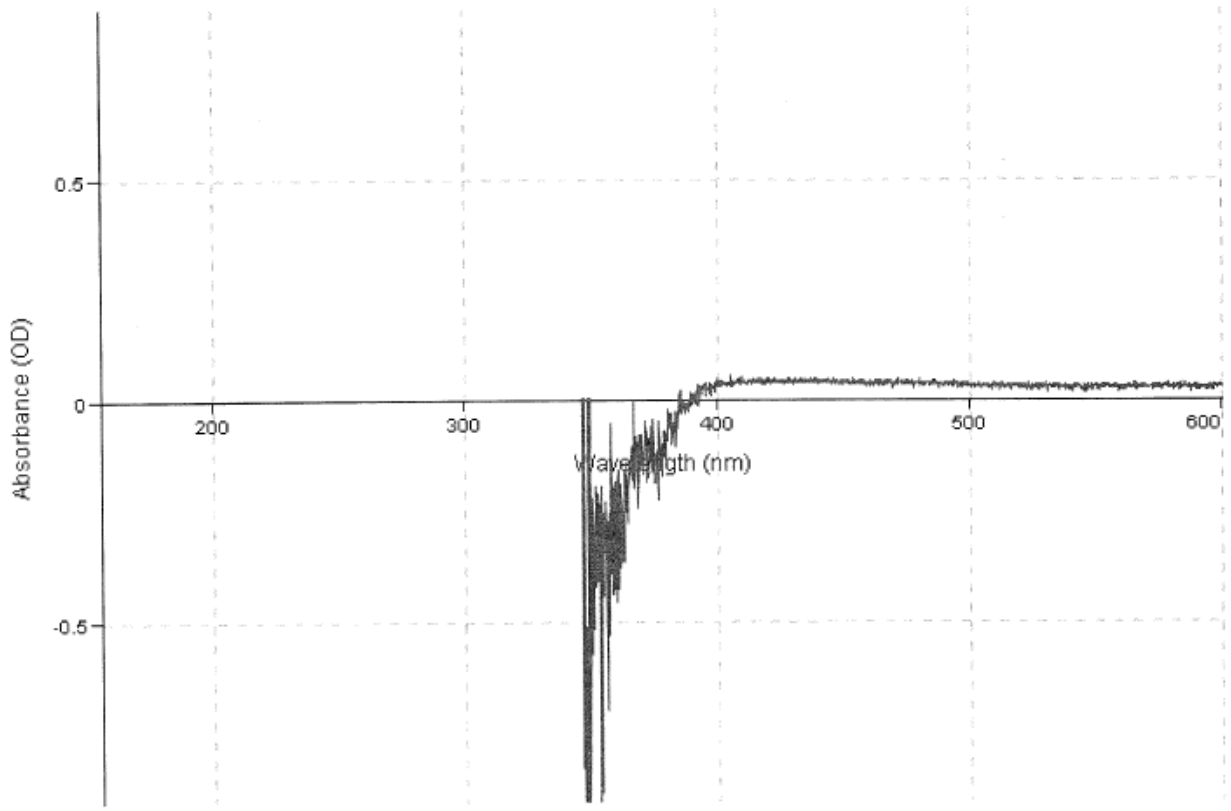
Tween 20 in H2O



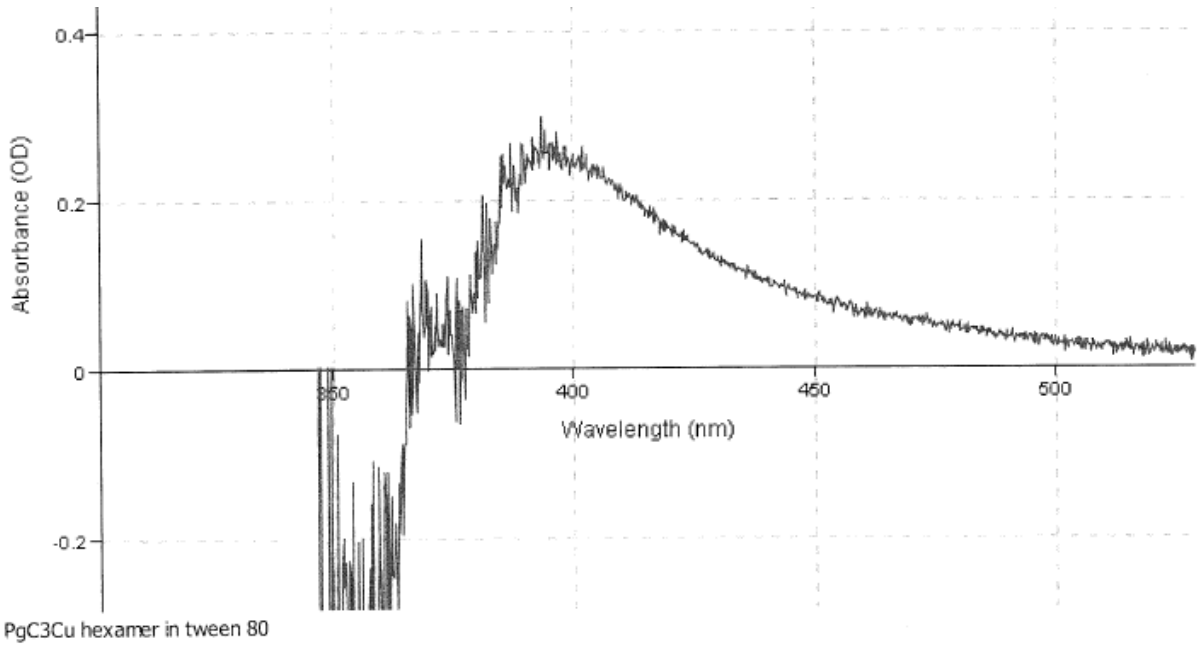
PgC3Zn in H2O



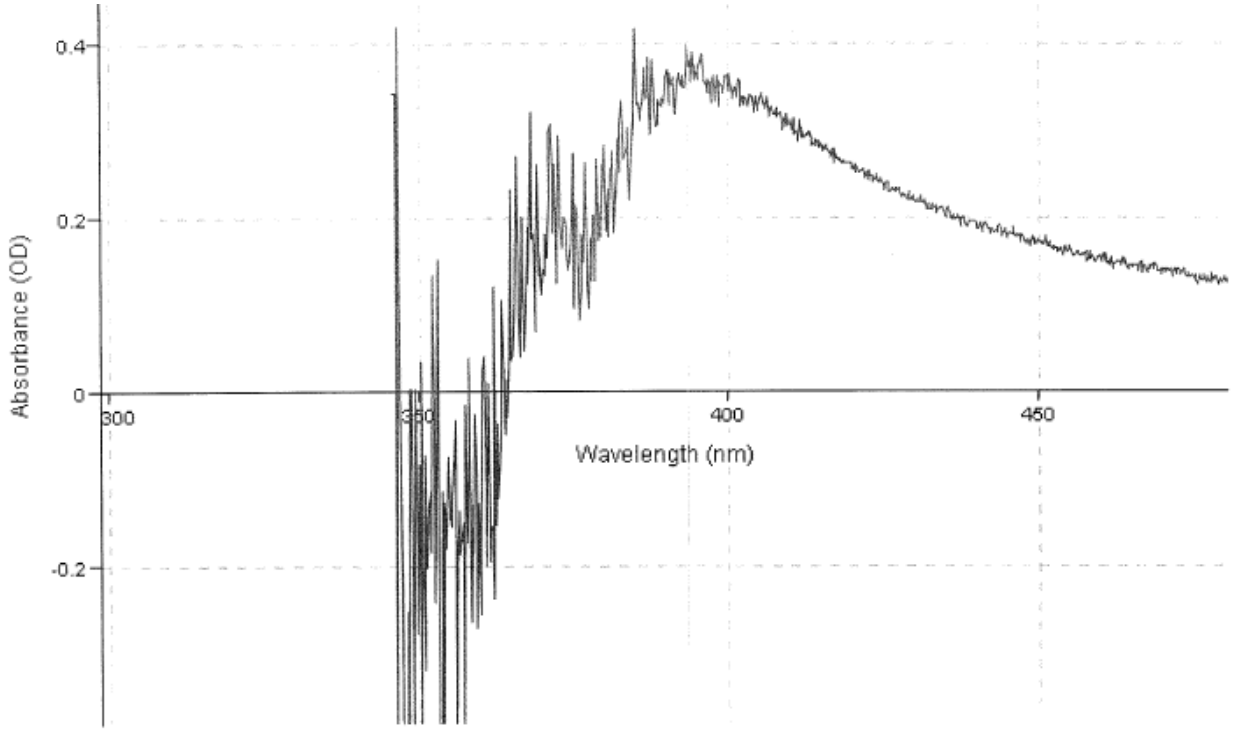
PgC3Zn dimer in Tween 80



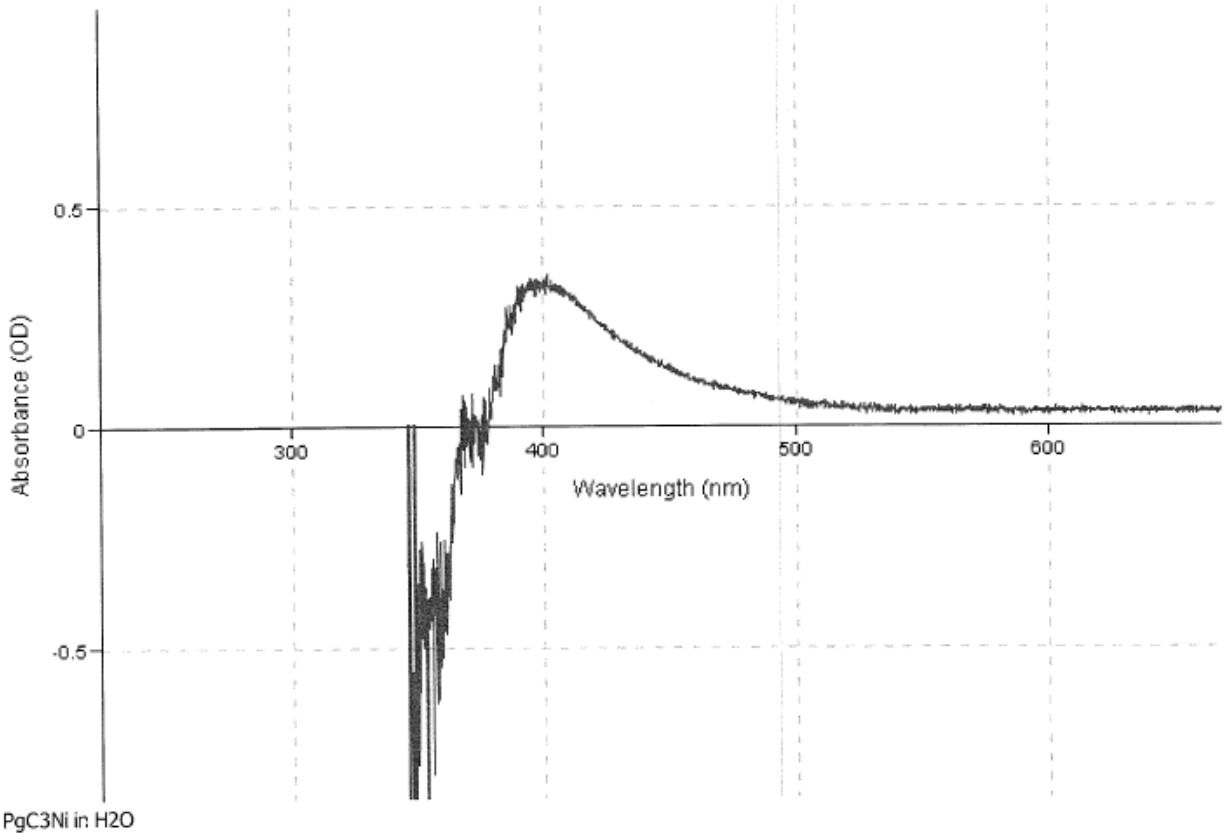
PgC3Cu hexamer in H2O



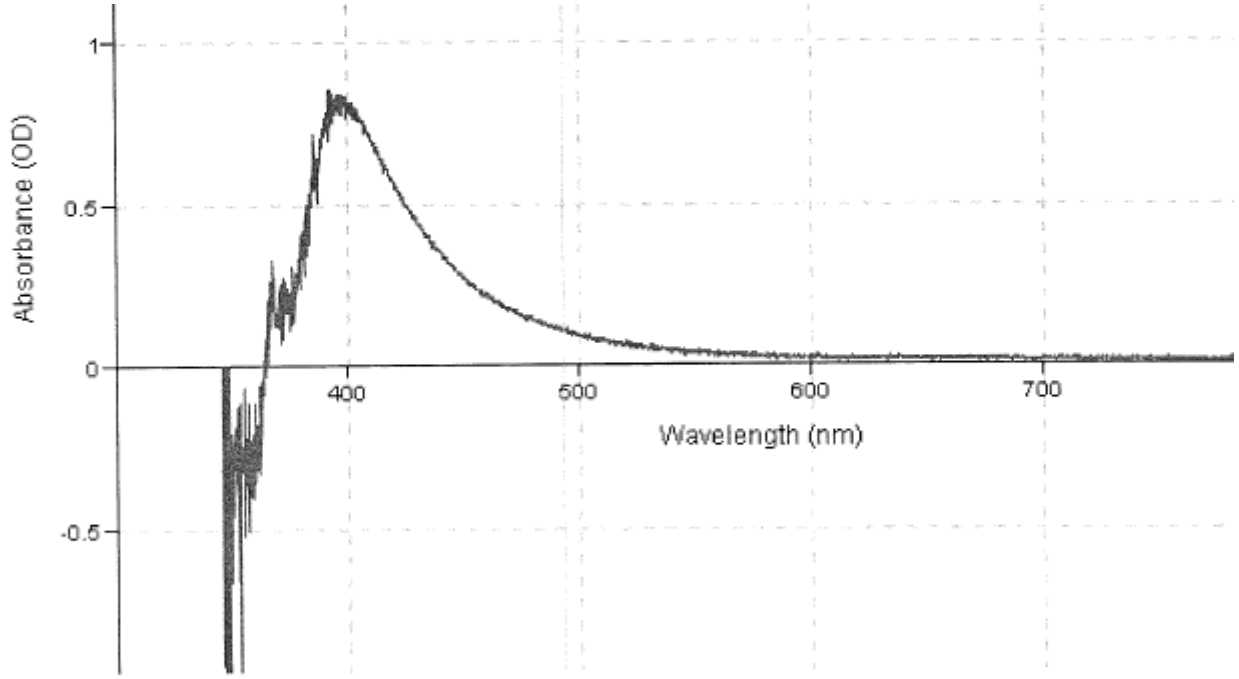
PgC3Cu hexamer in tween 80



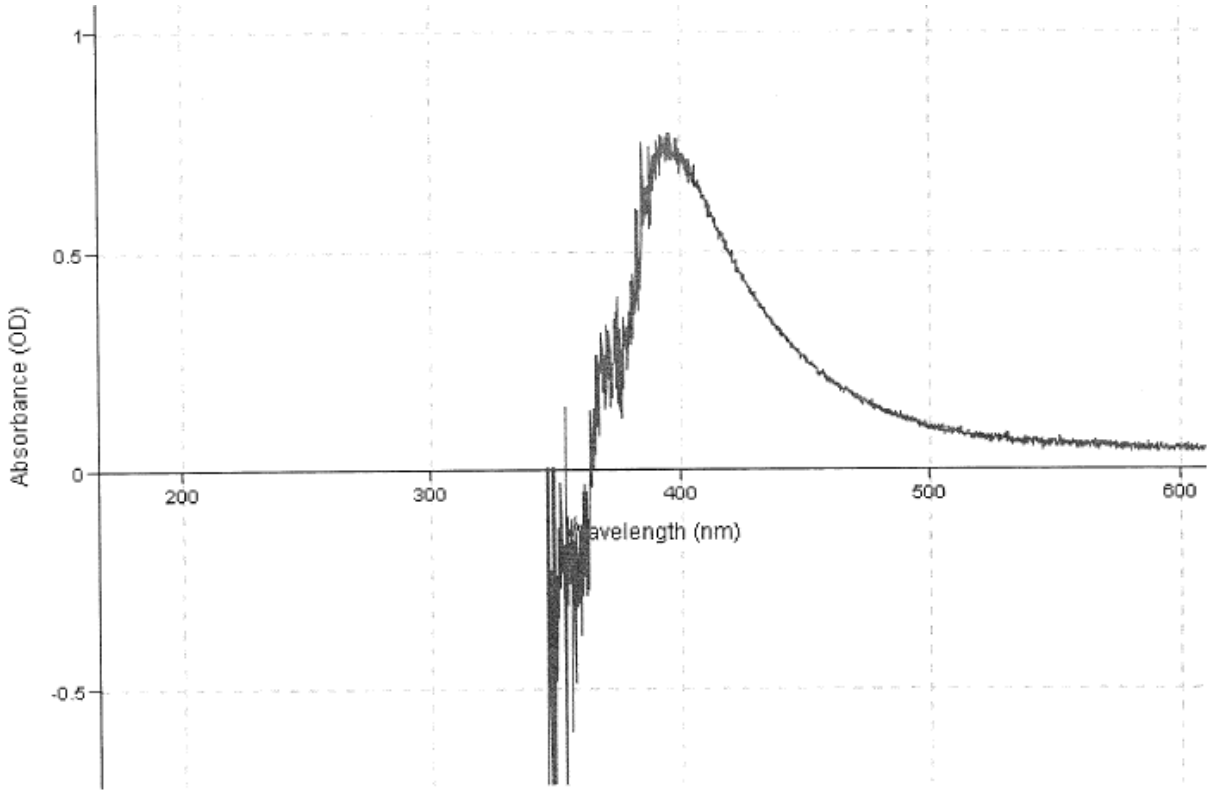
PgC3Cu hexamer in Tween 20



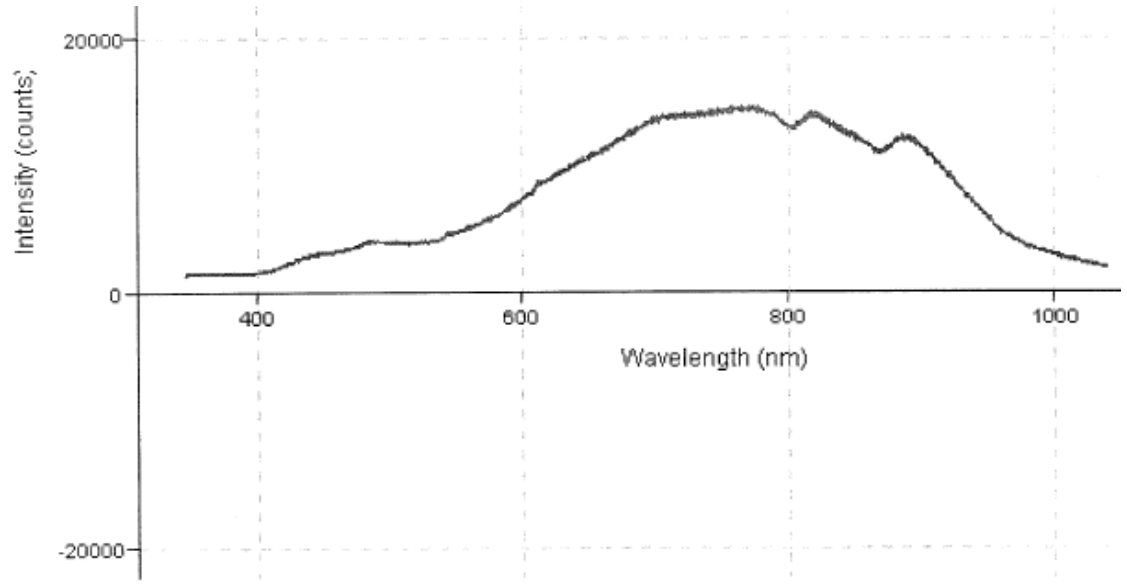
PgC3Ni in H2O



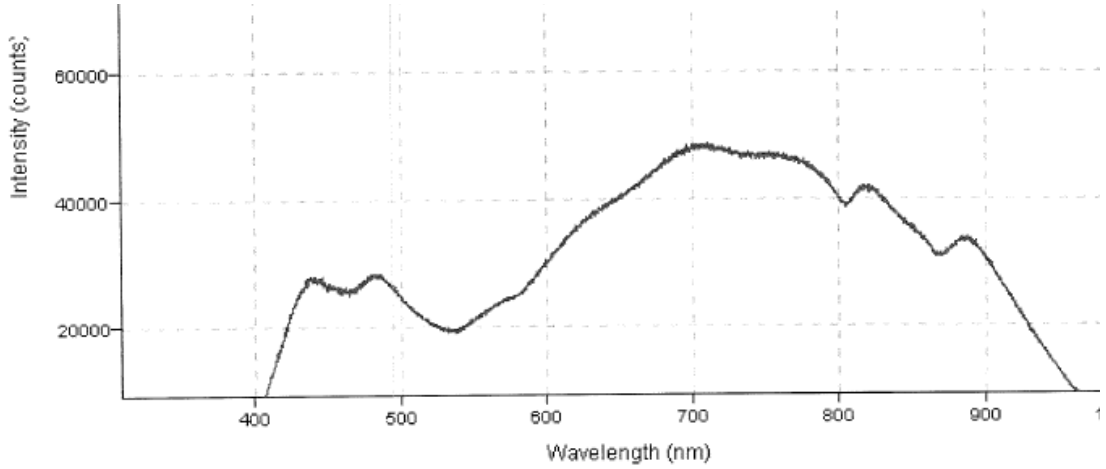
PgC3Ni hexamer in Tween 80



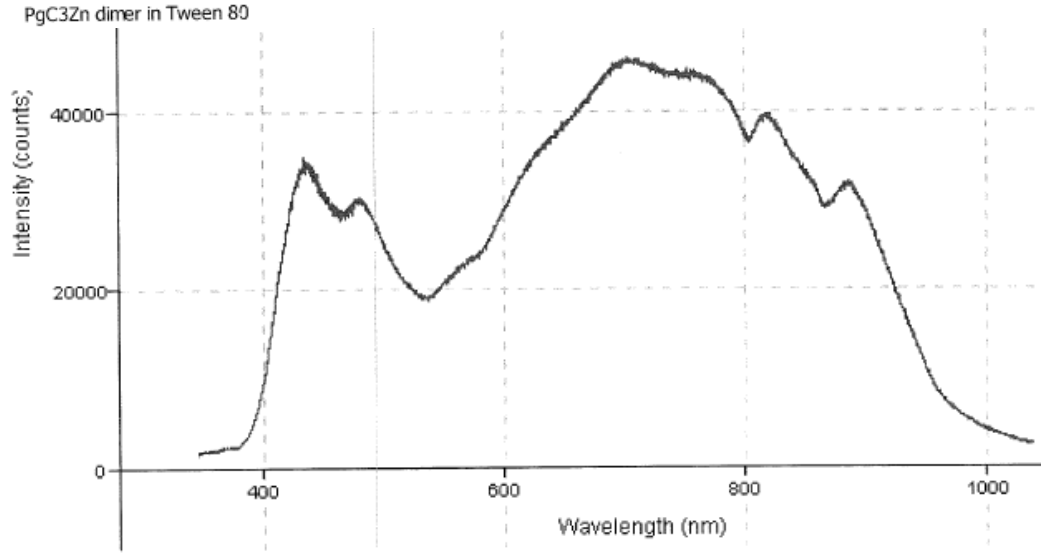
PgC3Ni in Tween 20



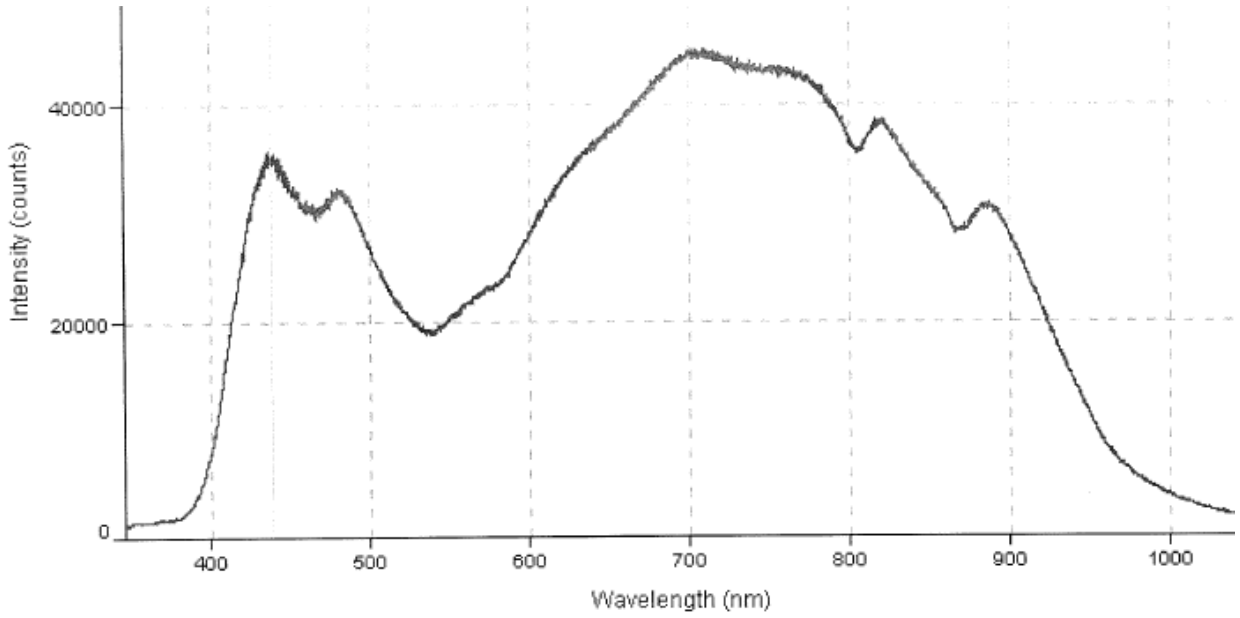
PgC3Zn dimer in Tween 20



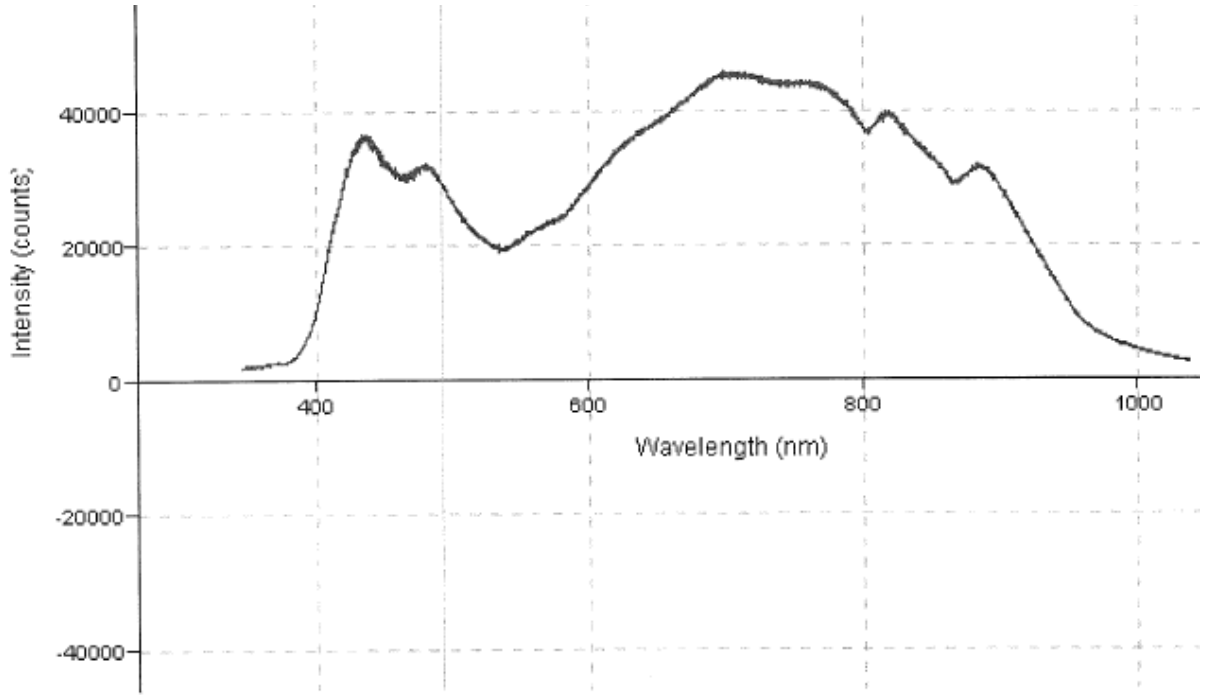
PgC3Zn dimer in Tween 80



PgC3Zn in H2O



Tween 20 in H2O



Tween 80 in H2O