Hierarchical organization of a robust porphyrin cage self-assembled by hydrogen bonds

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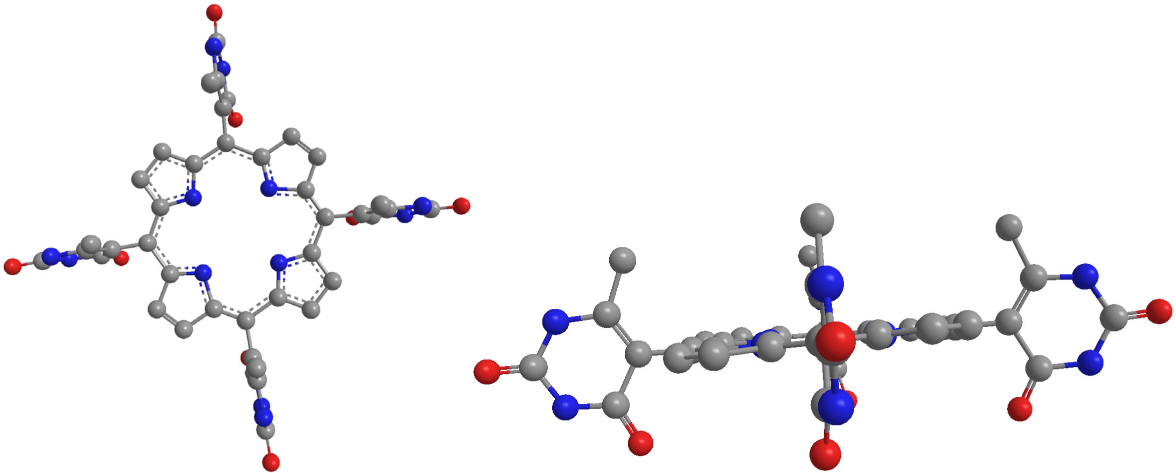


Scheme ESI-1. 3-dimensional structures of porphyrin **1a,** from Chem 3D ® showing the α^4 atropisomer.

Experimental Procedures

Materials and Methods. ^1H and ^{13}C Spectra were recorded in a Brüker Avance 500 MHz spectrometer. Mass spectrometry analyses were performed at the CUNY Mass Spectrometry Facility at Hunter College by electrospray ionization on an Agilent Technologies G6520 Q-TOF instrument and Agilent 1200 HPLC system. The electrospray ionization was done in methanol, with 0.1% formic acid. UV-visible spectra were recorded on a Varian Bio3 spectrophotometer. Steady-state fluorescence spectra and fluorescence lifetimes were measured with a Fluorolog τ3 TCSPC (time correlated single photon counting) from Jobin-SPEX Instrument S. A., (Horiba Scientific. Inc.) Dynamic light scattering (DLS) used a Precision Detector PD2000DLS Cool-Batch instrument in batch mode at 25 ^oC to determine size of the aggregates and cage. All reagents were obtained from commercial sources and used without purification. 5-Formyl-6-methyluracil and 1-ethoxymethyl-5-formyl-6-methyluracil were synthesized according to the previous literature.[1-3] Variable temperature NMR measurements were performed from the range 279 K to 323 K.

AFM. All samples were prepared in the following manner: freshly cleaved sheets of mica, approximately 2.5 x 2.5 cm, were placed in a clean Petri dish on a flat surface. For each sample, the given solution was drawn up into a pipette, and then a single drop (~0.5 mL) was drop cast onto a mica square. In the voids between the samples, dry THF was deposited via pipette, taking care that the THF did not contact any of the samples. A watch glass was then placed over the Petri dish, sealing the environment so the THF evaporated slowly. The samples were allowed to sit for 24 hrs, and then examined using an Asylum Research MFP-3D™ Stand Alone AFM in contact mode under ambient conditions. Images collected from the AFM were analyzed using a program called "WSxM 4.0 Develop 11.4", developed by Nanotec Electronica S.L. All samples were imaged with a Park silicon nitride tip (nominal $k = 0.1\ N\ m^{-1}$) in contact mode. Chem 3D estimates of the cage size are about 3.5 nm from bis(decyl)melamine -CH_3 to the opposite bis(decyl)melamine -CH_3, and 2.8 nm from top porphyrin face to opposite porphyrin face. The conformation of the alkyl groups, both on the uracyl and the melamine, is not known, so sizes are estimated for the extended conformations. Secondly, since these are not rigid or packed into rigid matrices, the AFM will not readily differentiate the vertical sizes between the cages formed from porphyrin **1** versus porphyrin **2**.

Photophysical Properties. The porphyrinoids **1a**, and **1b** are poorly soluble in dry THF, while **2a** and **2b** have better solubility in this solvent. The solutions were 38-42 μM in porphyrin. To accelerate the dissolution of **1a** and **1b** for the H-bond formation with bis(decyl)melamine, the solutions were sonicated for ca. five minutes and then transferred to a 3.5 mL quartz cuvette. N_2 gas was then purged through the mixture solution for ca. 10 minutes to make sure the complete removal of air or moisture from the solution. The 1.00 cm cuvette was then sealed with Teflon cap and wrapped with parafilm to make sure the system is closed. The UV-visible absorption spectra, fluorescence emission spectra, and lifetime measurements were recorded at room temperature for a few days until an equilibrium was observed. TCSPC fluorescence life time measurements used a 405 nm NanoLED laser, average power 13.6 pJ/pulse with a source pulse width <200ps to excite the molecules, and ~200 ps is the instrument response. The detection monochrometer was set at 405 nm with a 2 nm band-pass. The data was fit with the program available with the instrument. The decay was recorded at 651 nm. The solutions were then heated continuously for couple of hours and spectra were recorded. The UV-visible and emission spectra of all the porphyrins by themselves exhibit the aggregation but do not change after one day (ESI 34-39).

Synthesis of Porphyrin 1b

Pyrrole (69.5 µL, 1.0 mmol) and 5-Formyl-6-methyluracil (158 mg, 1.0 mmol) and zinc acetate (109.8 mg, 0.50 mmol) were added to a boiling mixture of acetic acid (7.5 mL) and nitrobenzene (5.0 mL). The reaction mixture was refluxed for 10 h while monitoring the yields spectroscopically, and then taken to dryness under vacuum. The resulting solid was purified by column chromatography, eluting with ethyl acetate/ methanol/ acetic acid (7:3:1) to yield 17 mg (8 %) of **1**. Chromatographic purification enriches the α^4 and $\alpha^3\beta$ atropisomers. ^{1}H NMR (DMSO-d_6) δ11.5 (br, d, 8H), 9.50 (s, 8H), 2.50 (s, 12 H); ^{13}C (DMSO-d_6) δ 41.84, 110.60, 113.38, 113.41, 131.70, 150.77, 150.81, 152.26, 166.25. HRMS calcd. for $C_{40}H_{28}N_{12}O_8Zn$ (M+H)+ 869.1523, found 869.1514.

Synthesis of Porphyrin 2b

The starting aldehyde was synthesized according to the previous literature. Pyrrole (69.5 µL, 1.0 mmol) and 1-ethoxymethyl-5-formyl-6-methyluracil (212 mg, 1.0 mmol) and zinc acetate (109.8 mg, 0.50 mmol) were added to a boiling mixture of acetic acid (7.5 mL) and nitrobenzene (5.0 mL). The reaction mixture was refluxed for 10 h while monitoring the yields spectroscopically, and then taken to dryness under vacuum. The resulting solid was purified by column chromatography, eluting with ethyl acetate/ methanol (9:1) to yield 15 mg (5 %) of **2**. Chromatographic purification enriches somewhat the α^4 and $\alpha^3\beta$ atropisomers. ^{1}H NMR (MeOD-d_4) δ 9.22 (s, 8H), 5.65 (m, 8H), 3.86 (m, 8H), 2.51 (m, 12H), 1.31(m, 12H). ^{13}C NMR (MeOD-d_4) δ 12.83, 14.48, 54.63, 63.24, 71.86, 129.61, 149.23, 163.24, 189.5. HRMS calcd. for $C_{52}H_{52}N_{12}O_{12}Zn$ $(M)^{+\cdot}$ 1100.3119, found 1100.3112.

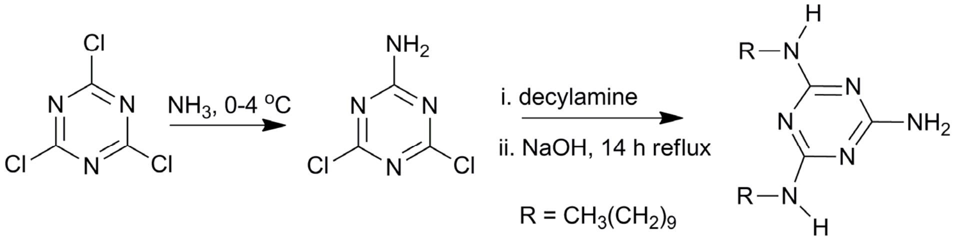
Free base porphyrins 1a and 2a. Porphyrin **2b** (15 mg, 13 µmol) were dissolved in THF, water and conc. HCl. The mixture was stirred for 30 min, the mixture was poured into water and $(NH_4)_2CO_3$ was added until the pH is 6, the porphyrin products were extracted with ethylacetate. The combined organic extract was washed with water and brine and dried over Na_2SO_4 and then porphyrin was precipitated with ethylacetate/hexane to give the free base porphyrin **2a** (12 mg, 90 % yield). Porphyrin **1b** (15 mg, 17 µmol) were dissolved in THF, acetic acid and conc. HCl. The mixture was stirred for 30 min, the mixture was poured into water and $(NH_4)_2CO_3$ was added until the pH is 6. The porphyrin was precipitated from solution to give **1a** (12 mg, 90% yield).

Atropisomers. Porphyrins **1** and **2** shows atropisomerism because of the steric hindrance to rotation of the uracyl-porphyrin bond due to interactions between the uracyl 2-carbonyl and 6-methyl groups and the pyrrole βH. The thermodynamics of atropisomerization was determined for **2b** in MeOD-d_4. The ^{1}H NMR spectra of porphyrin **2** has distinct resonances for the uracyl 6-methyl due to ring current effects and the 1-N methylene groups. There should be six resonances for both the 6-methyl near 2 ppm, and the 1-N methylene group, observed as complex multiplets near 5 ppm. The ratio of the resonances for the 6-methyl group was used to determine the ratio of the four rotamers; which in the initially prepared porphyrin was approximately the expected 1:4:2:1 for αααα, αααβ, ααββ, and αβαβ. The rotational barrier was determined for porphyrin **2b** by doing the variable temperature NMR from 5 °C to 50 °C in methanol-d_4.[4] The value of K was determined by shift in the (N-CH_2-O) protons. The equilibrium constant was determined by a Van't-Hoff plot (ln K versus 1/T) and the $\Delta G^\ddagger$ was found to be about 123 kJ/mol for **2b**.[5, 6] The $\Delta G^\ddagger$ for the free base is typically less by about 20 kJ/mol because the metalloporphyrin is more rigid. The poor solubility of porphyrins **1a** and **1b** made similar analysis difficult, but the barriers should be about the same. MALDI mass spectrometry reveals the starting components but not the cages. Note that one uracyl methyl resonance is observed for the cages (ESI 28-29).

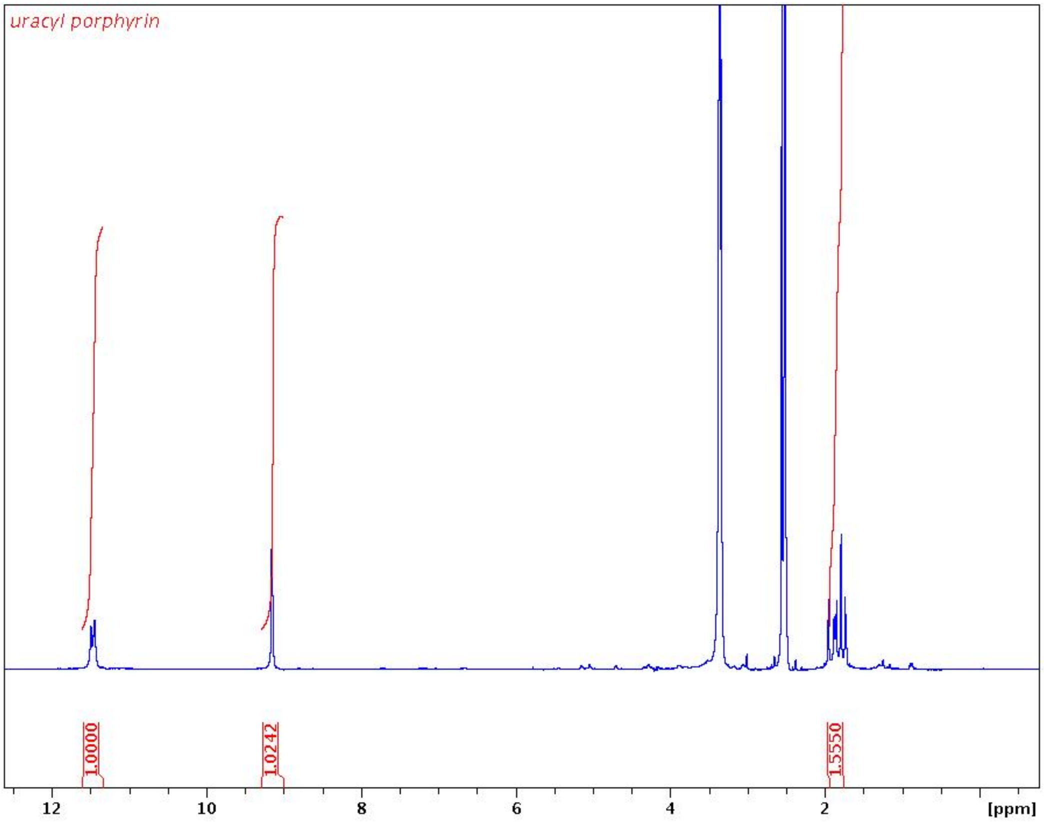
2,4-di(*n*-decylamino)-6-amino-1,3,5-triazine. bis(decyl)melamine, was prepared similarly to literature methods[7-9] from 2-Amino-4,6-dichloro-1,3,5-triazine, which was prepared from cyanuric chloride (Scheme ESI-2). [10]

Authorship. S. Singh: synthesis, NMR studies; A. Aggarwal: DLS, photophysical studies and corresponding figures; C. Farley: photophysical studies; B.A. Hageman: AFM studies; C.M. Drain and J.D. Batteas: data analysis and interpretation, manuscript preparation. We thank Matthew Jurow for help with the AFM studies.

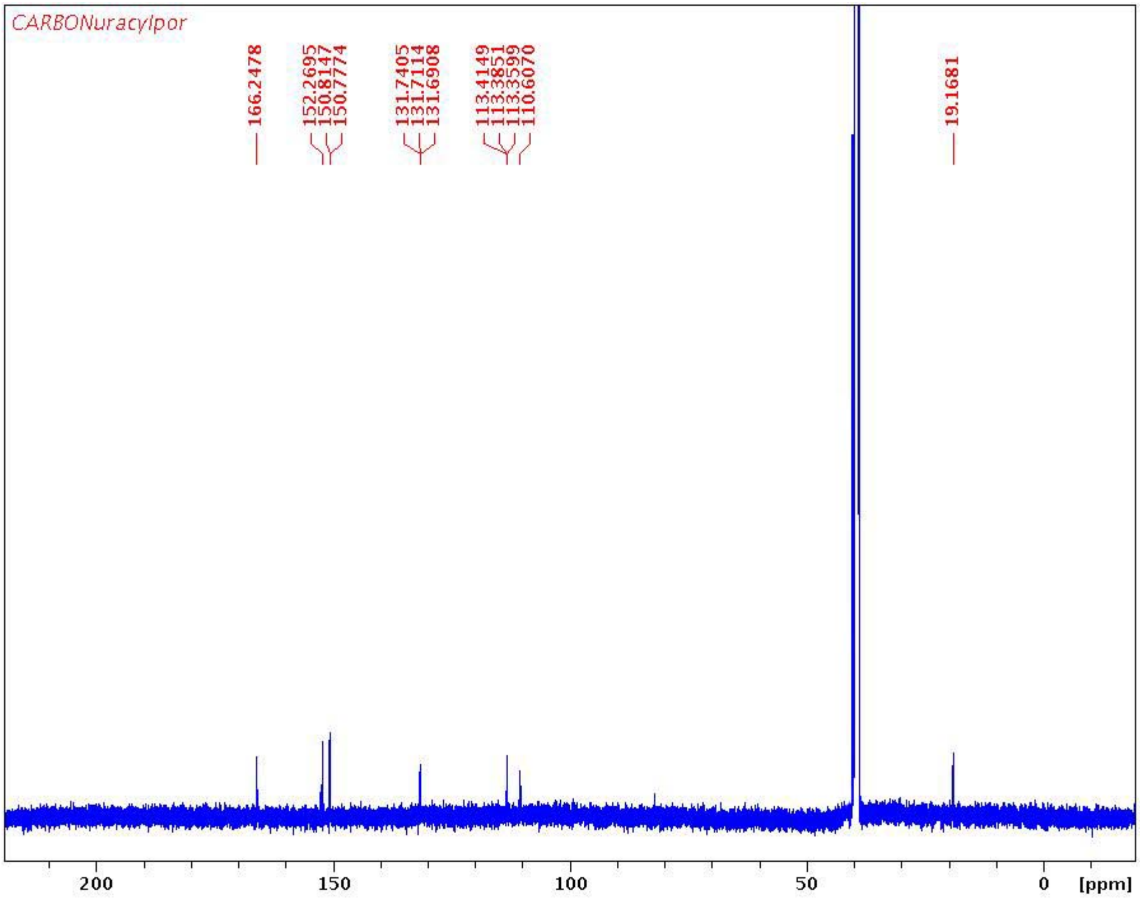
N2, N4-bis(decyl)melamine



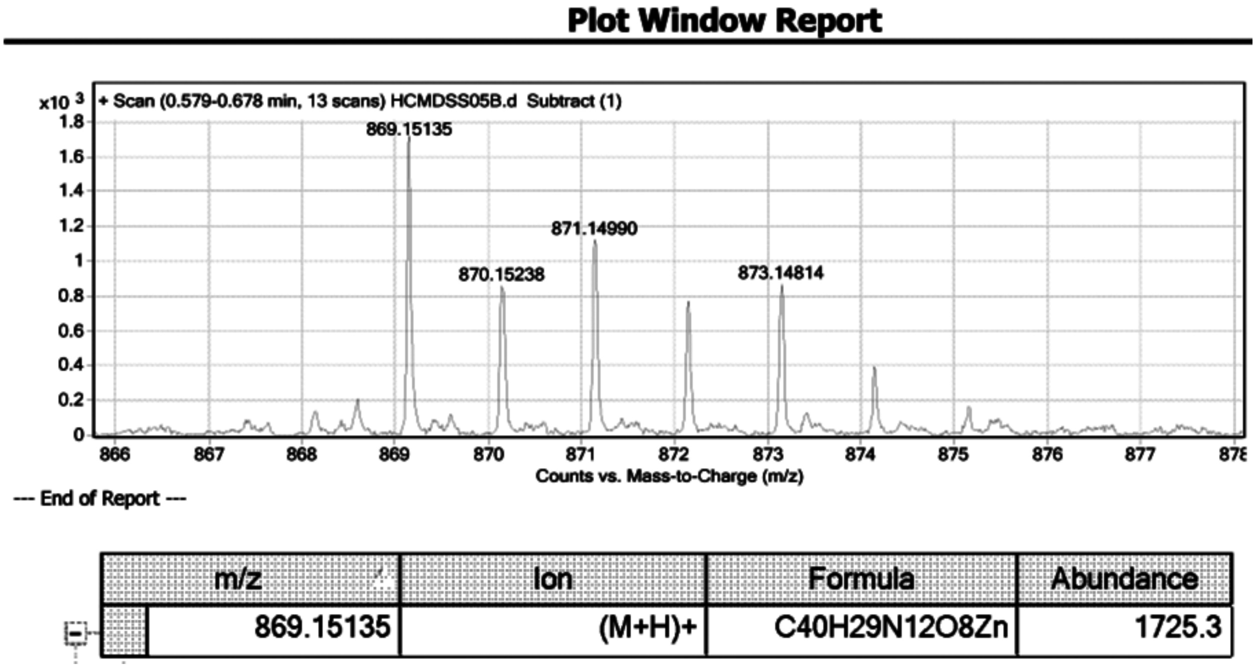
Scheme ESI-2. bis(decyl)melamine synthesis.



ESI 1: ^{1}H NMR of porphyrin **1b** in DMSO-d$_6$.



ESI 2: ^{13}C NMR of Porphyrin **1b** in DMSO-d_6.



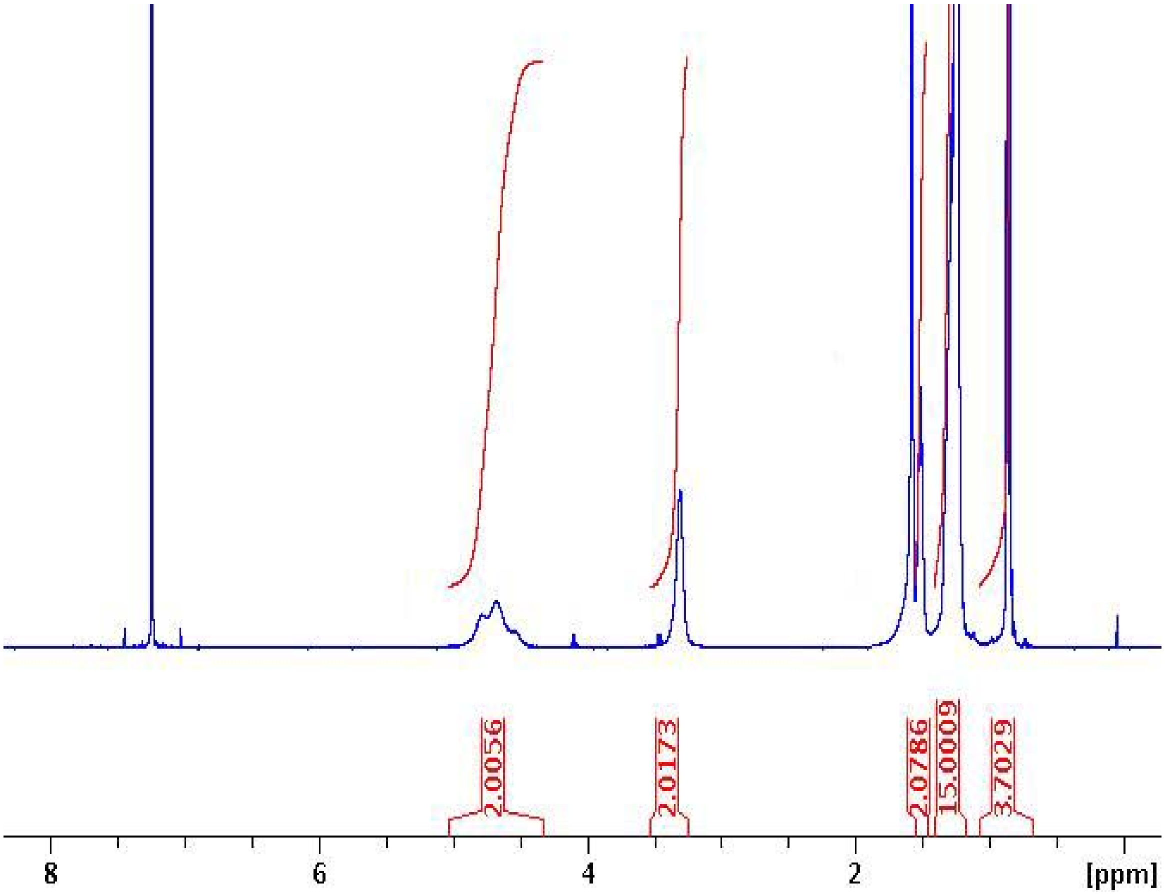
Plot Window Report

+ Scan (0.579-0.678 min, 13 scans) HCMDSS05B.d Subtract (1)

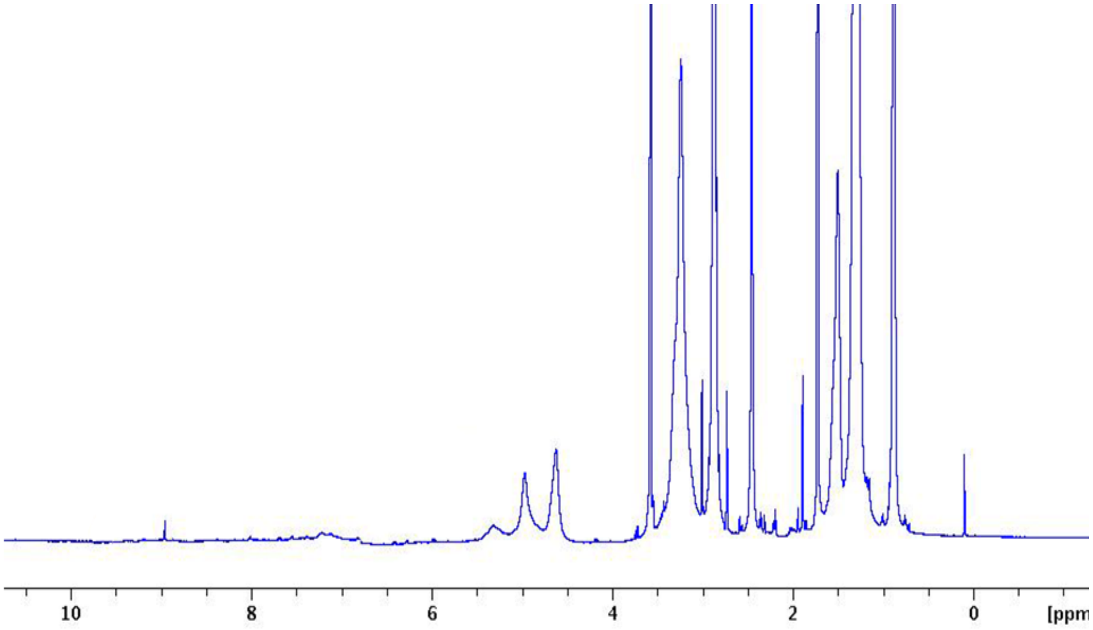
--- End of Report ---

m/z	Ion	Formula	Abundance
869.15135	(M+H)+	C40H29N12O8Zn	1725.3

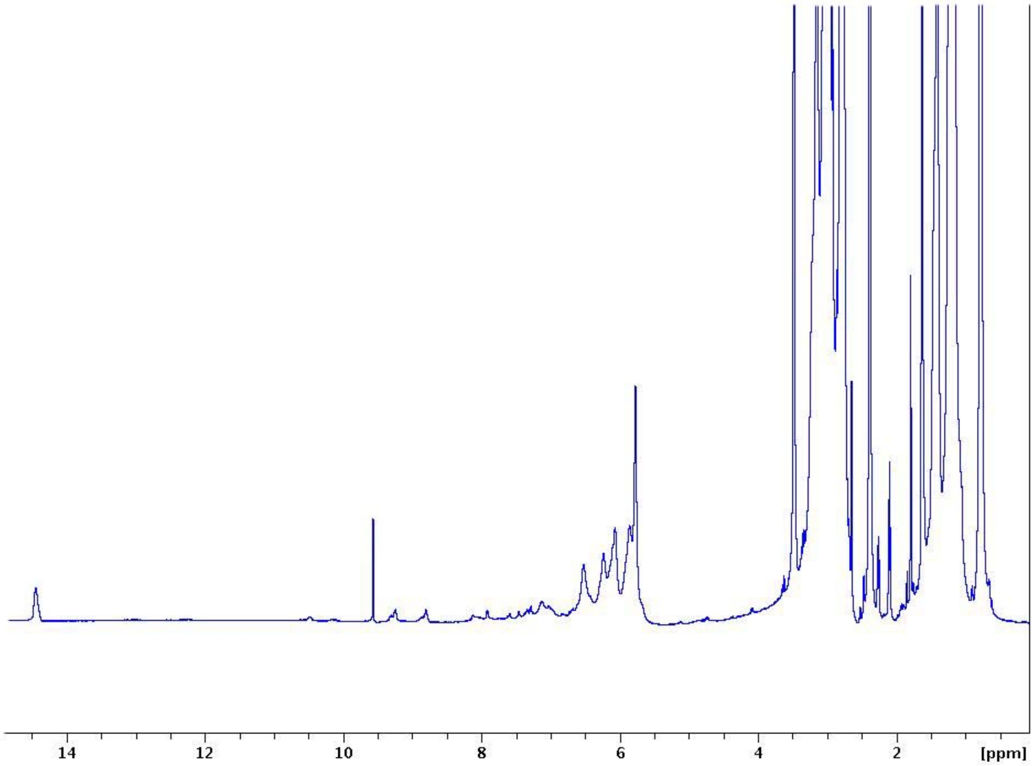
ESI 3: Mass spectrum of Porphyrin **1b**



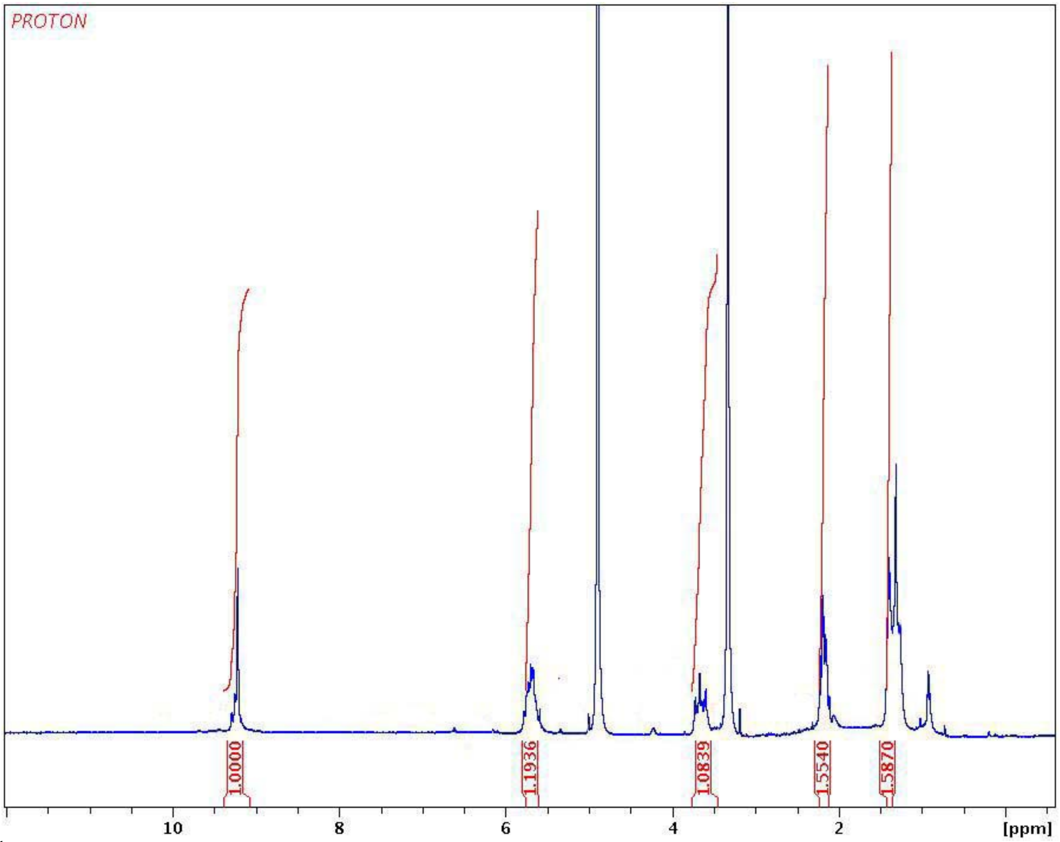
ESI 4: NMR of bis(decyl)melamine in $CDCl_3$.



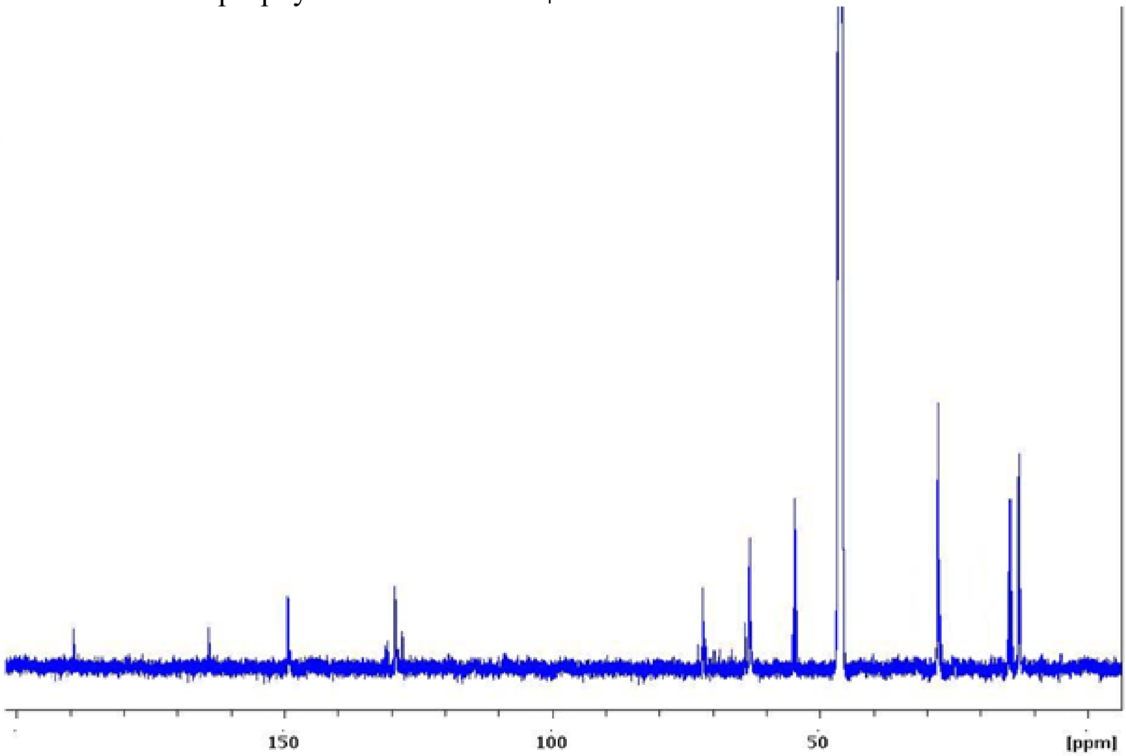
ESI 5: Day 1 NMR of melamine and porphyrin **1b** in dry THF in ratio 4:2 respectively.



ESI 6: Day 14 NMR of melamine and porphyrin **1b** in dry THF in ratio 4:2 respectively.



ESI 7: ^{1}H NMR of porphyrin **2b** in MeOD-d_4 solvent.

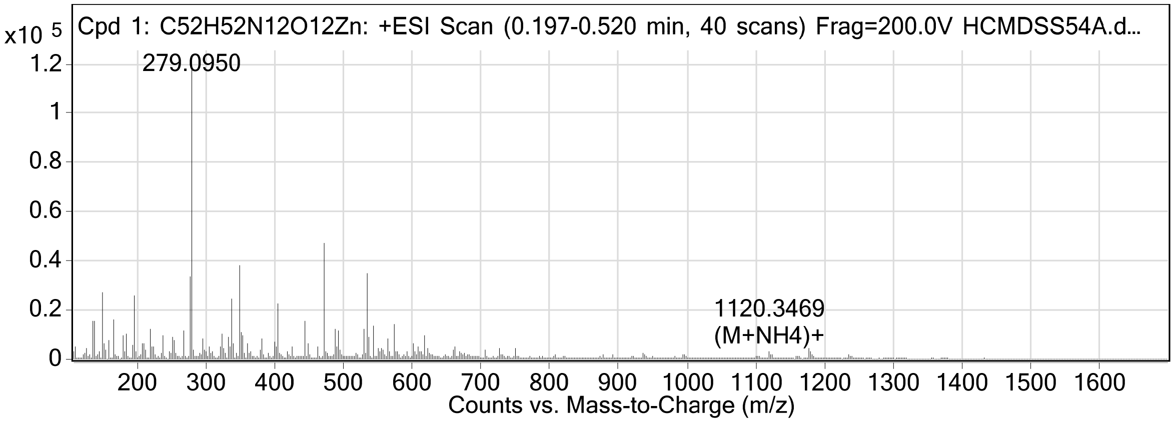


ESI 8: ^{13}C NMR of porphyrin **2b** in MeOD-d_4 solvent.

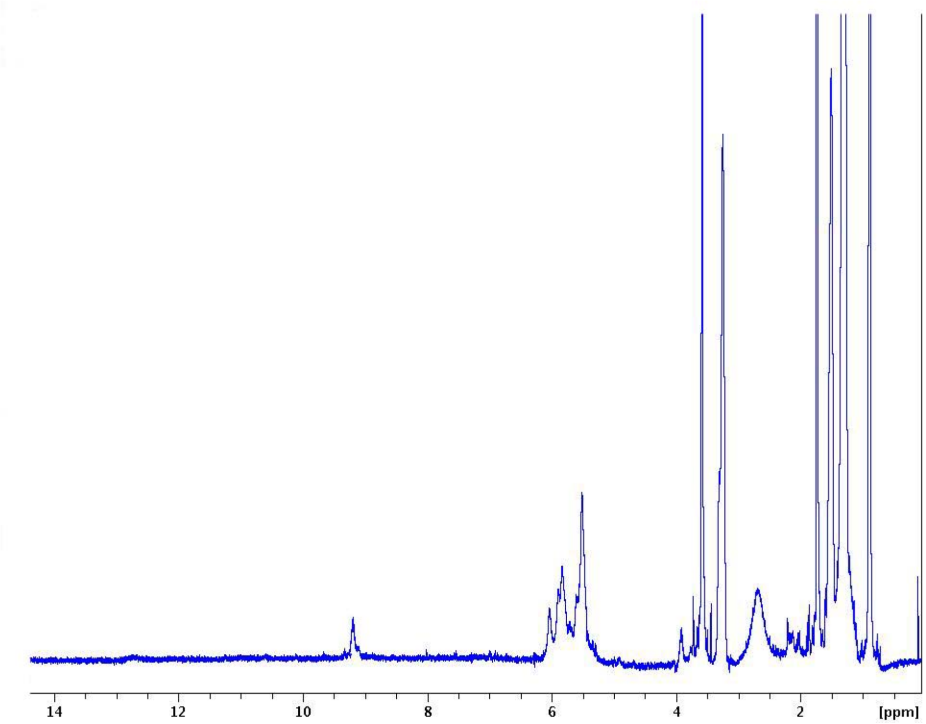
Data File	HCMDSS54A.d	**Sample Name**	EthoxyZnPor
Sample Type	Sample	**Position**	P1-A2
Instrument Name	Instrument 1	**User Name**	
Acq Method		**Acquired Time**	9/17/2010 7:28:46 PM
IRM Calibration Status	Some Ions Missed	**DA Method**	HCEmpirical1.m
Comment	EM=1100.3119 EM=HC ESI Pos Small Molecule No HPLC.m		

Compound Table

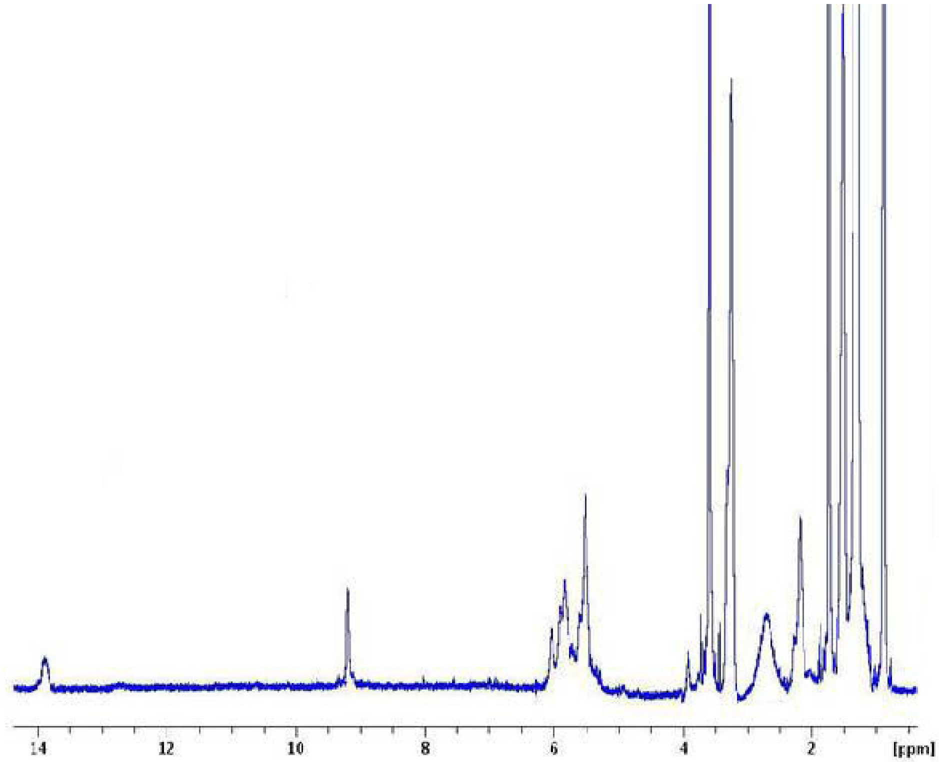
Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C52H52N12O12Zn	**0.264**	**1100.3122**	**2913**	**C52H52N12O12Zn**	**1100.3119**	**0.24**



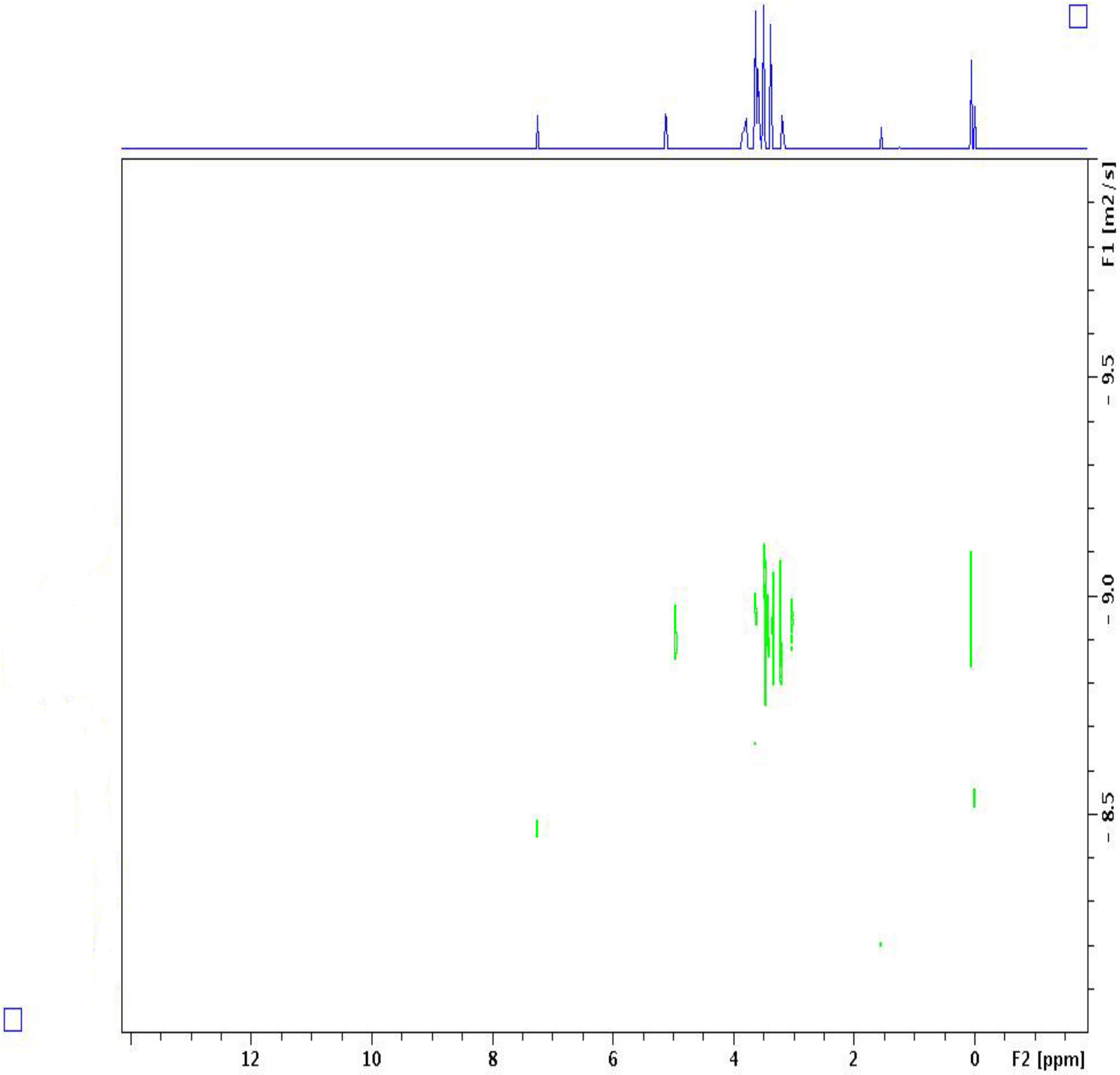
ESI 9: Mass spectrum of porphyrin **2b**.



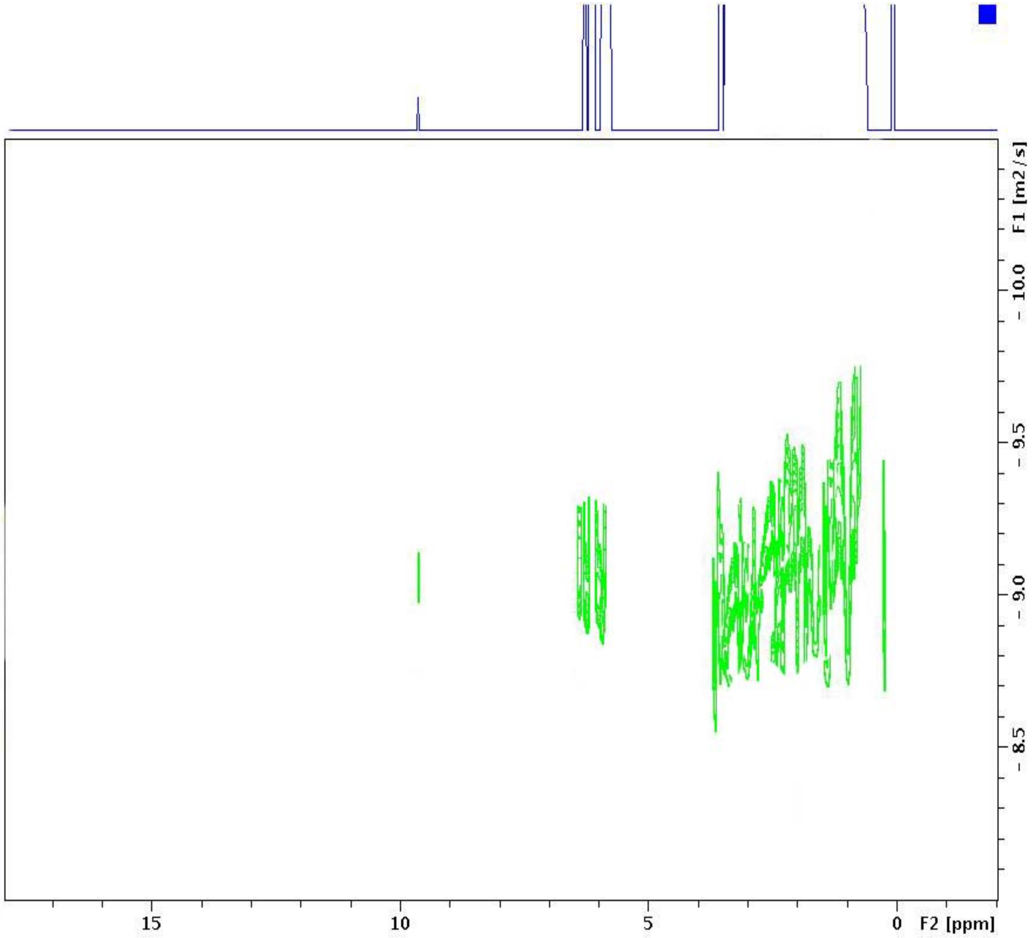
ESI 10: ^{1}H NMR of Porphyrin **2b** + melamine; day 1 in THF-d_8.



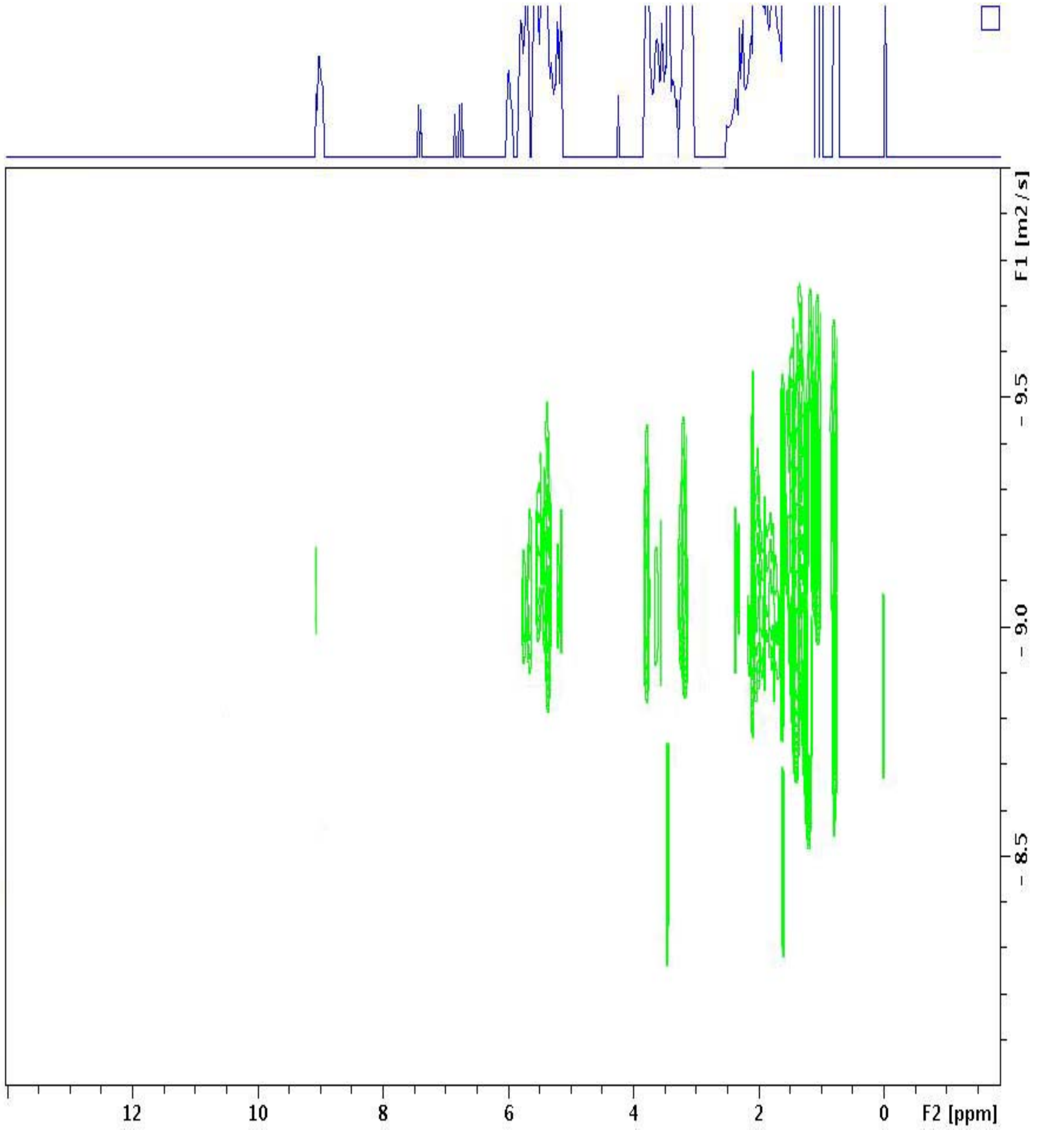
ESI 11: ^{1}H NMR of Porphyrin **2b** + melamine; day 10 in THF-d_8.



ESI 12: 2D DOSY spectrum of cyclodextrin in $CDCl_3$.



ESI 13: 2D DOSY spectrum of porphyrin **1b** + melamine in THF-d_8 solvent.



ESI 14: 2D DOSY spectrum of Porphyrin **2b** + melamine in THF-d_8 solvent.

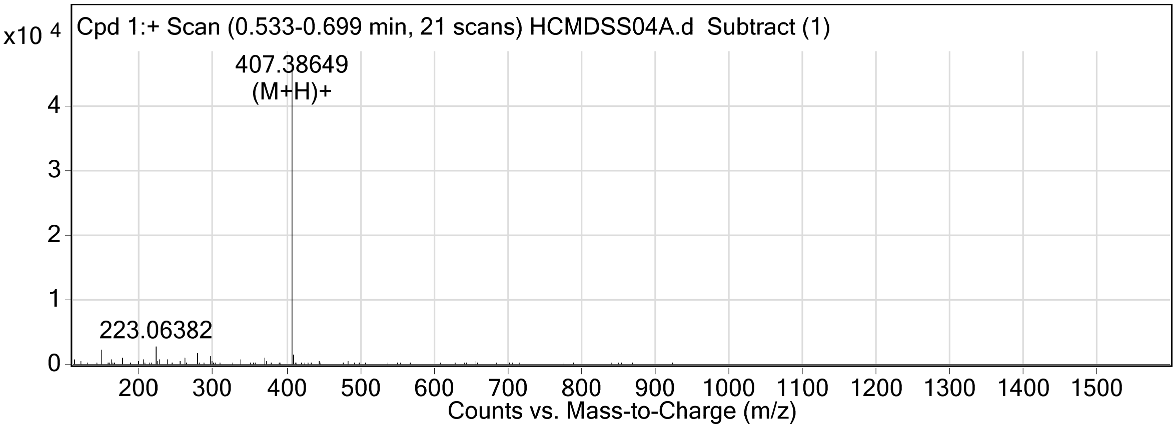
Data Filename	HCMDSS04A.d	**Sample Name**	Alkylated Melamine
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	
Acq Method	HC ESI Pos Small Molecule No HPLC.m	**IRM Calibration Status**	Success
DA Method	HCEmpirical1.m	**Comment**	EM=406.38 M=HC ESI Pos Small Molecule No HPLC.m

Compound Table

Name	RT	Mass	Abund.	Formula	Tgt Mass	Diff (ppm)
Compound 1	0.6	406.37921	46202	C23H46N6	406.3784	2.01

Compounds

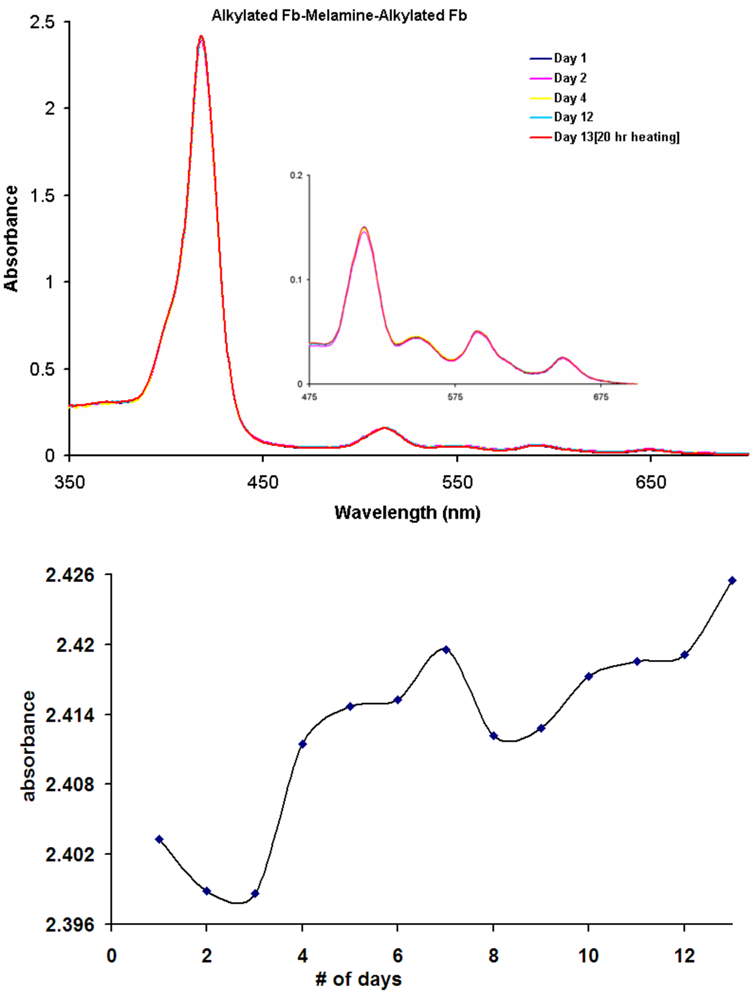
Name	RT	Algorithm	Mass
Compound 1	0.583	Find By Formula	406.37921



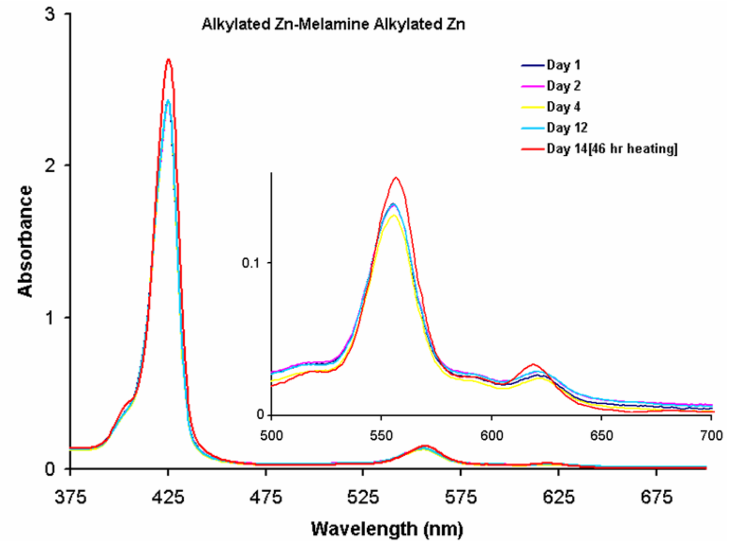
MS Spectrum Peak List

m/z	z	Abund.	Formula	Ion	Diff(ppm)
223.06382		2821			
407.38649	1	47484	C23H47N6	(M+H)+	2.01
408.38908	1	11471			

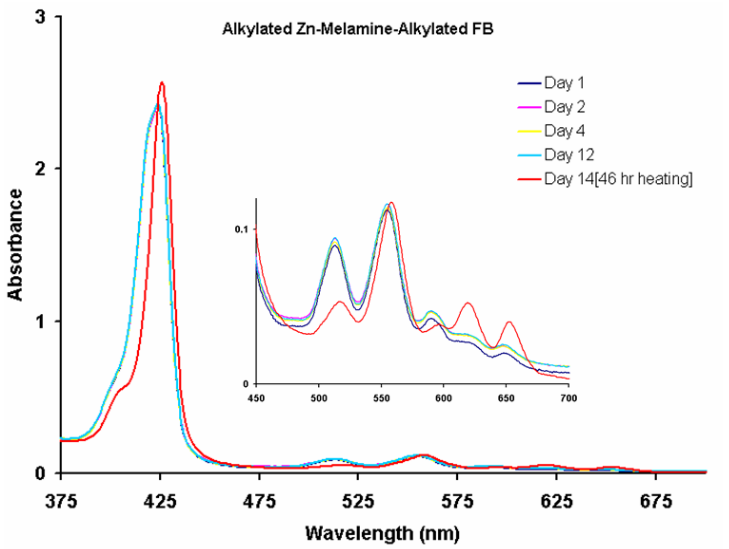
ESI-15. Mass spectrum of bis(decyl)melamine.



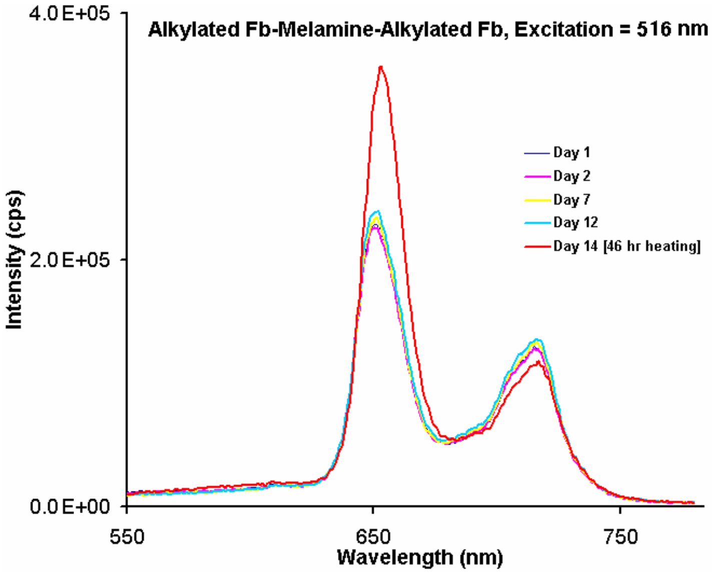
ESI 16: *Top:* UV-visible absorption spectra of the cage with the alkylated free base porphyrins (cage **2a-2a**) with melamine in dry THF. The concentration of porphyrins in solution was 42 µM. *Bottom:* the absorption intensity decreases slightly initially, indicating the association of the porphyrin into aggregates driven by the melamine, but after heating the sample at 45-47 ^{o}C for ~20 h, the absorption intensity increases, indicating the cage formation and increased solubility. The Soret band shifts to the red slightly for the solution containing the aggregates. In THF, the Soret band for **2a** is 422 nm and for the cage is at 424 nm.



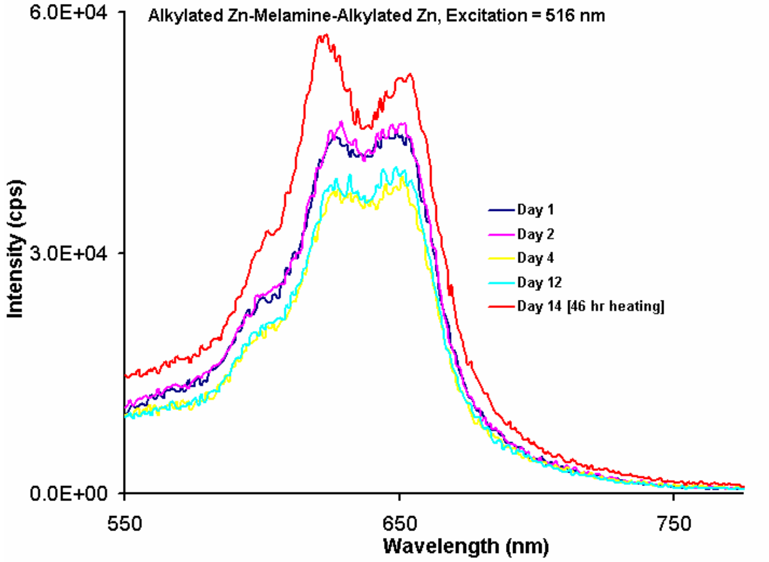
ESI 17: UV-visible absorption spectra of alkylated metalloporphyrins (cage **2b-2b**) with melamine in dry THF. The concentration of the porphyrins in solution was 39 µM. The initial absorption intensity decreases because of the association on the porphyrins into aggregates driven by the melamine. After heating the sample at 45-47 °C for couple of days the absorption intensity increases, indicating increased solubility and the formation of the cage. The Soret band initially shifts to the red by 1 nm, and somewhat broadens, as expected for aggregates. The Soret band for the **2b-2b** cage is at 424 nm.



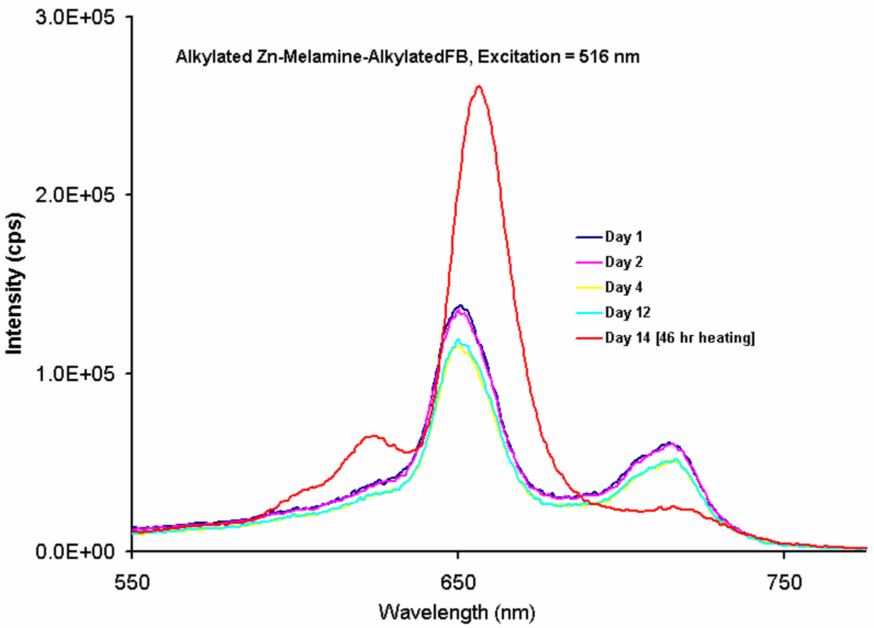
ESI 18: UV-visible absorption spectra of a 1:1 mixture of the alkylated free base- and metalloporphyrins (**2a** and **2b**) with melamine in dry THF. There is a 1:2:1 mixture of cages containing **2a-2a**, **2a-2b**, and **2b-2b**. The concentration of the porphyrins in solution was 38 µM. The absorption intensity initially decreases, indicating aggregate formation driven by the addition of the melamine. Upon heating the sample at 45-47 °C for couple of days, the absorption intensity increase, indicating increased solubility and formation of the cage. The Soret band for the mixture of supramolecular cages is at 425 nm.



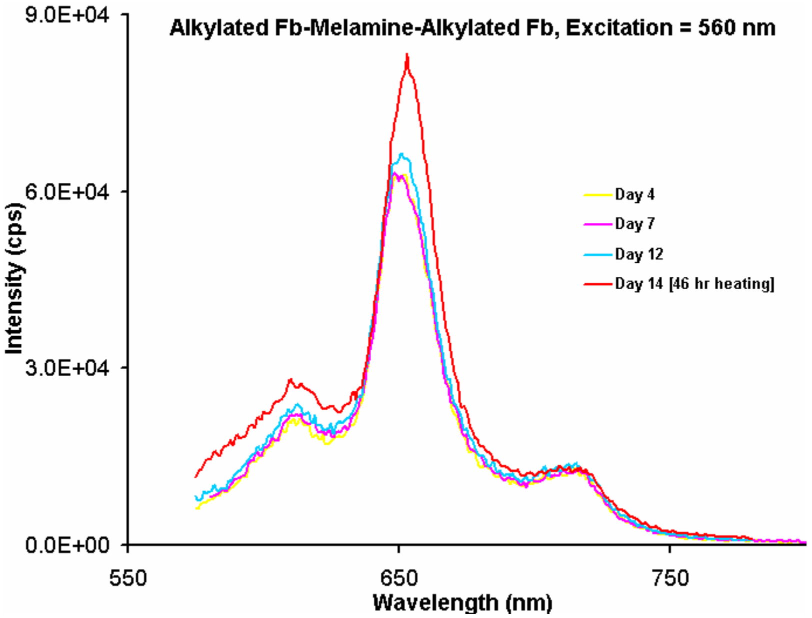
ESI 19: Fluorescence emission spectra of the alkylated free base cage (cage **2a-2a** with melamine) in dry THF (516 nm excitation where the OD = 0.15 and band pass = 2 nm). The concentration of porphyrins in solution was 42 μM (see figure 16). The emission spectra intensity increases as the initially formed aggregates evolve into the more soluble cage structure upon heating the sample for about three days at 45-47 °C. The emission peak shift to the red end by 3 nm.



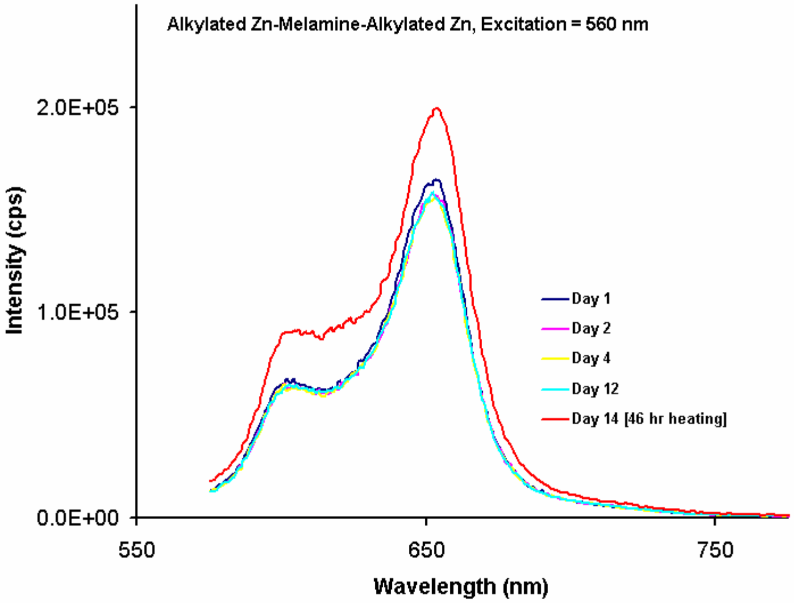
ESI 20: Fluorescence emission spectra of alkylated Zn-Zn (cage **2b-2b**) with melamine in dry THF. The mixture solution was excited at 516 nm where the OD = 0.04 and band pass = 2 nm. The emission spectra intensity increases as the initially formed aggregates evolve into the more soluble cage structure upon heating the sample for about three days at 45-47 °C.



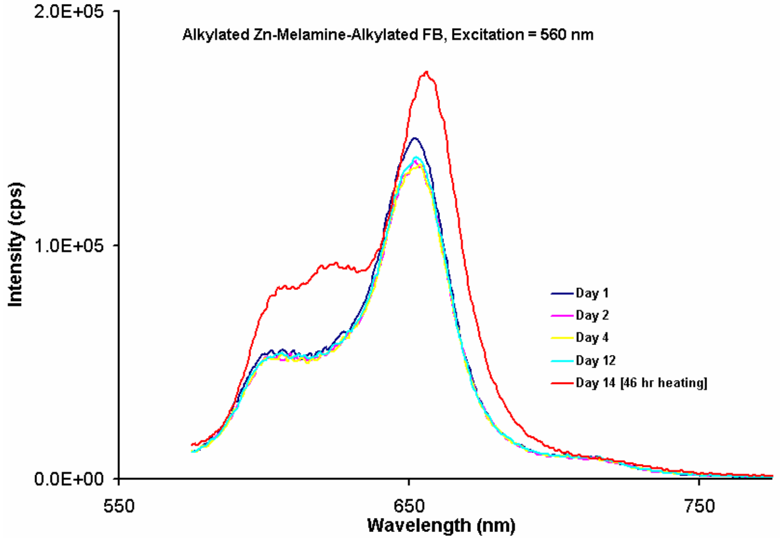
ESI 21: Fluorescence emission spectra of alkylated Zn-FB (cage **2a-2b**) with melamine in dry THF. There is a 1:2:1 mixture of cages containing **2a-2a**, **2a-2b**, and **2b-2b**. The mixture solution was excited at 516 nm where the OD = 0.09 and band pass = 2 nm. At 516 nm, **2a** absorbs ~5 times more than **2b**. The emission spectra intensity increases as the initially formed aggregates evolve into the more soluble cage structure upon heating the sample for couple of days at 45-47 ^{o}C. Since **2b** is less soluble than **2a** more of **2b** is observed upon formation of the cages relative to the aggregates.



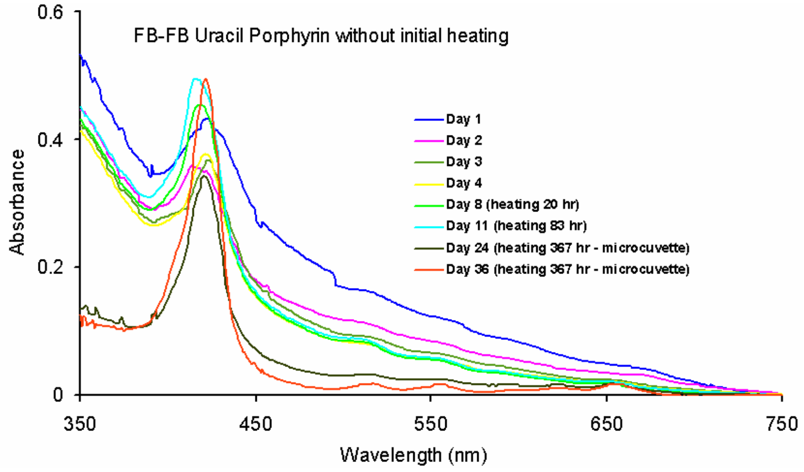
ESI 22: Fluorescence emission spectra of alkylated FB-FB (cage **2a-2a**) with melamine in dry THF. The mixture solution was excited at 560 nm where the OD = 0.04 and band pass = 2 nm. The emission spectra intensity increases as the initially formed aggregates evolve into the more soluble cage structure upon heating the sample for couple of days at 45-47 ^{o}C. The emission peak shifts to the red end by 4 nm on **2a-2a** cage formation.



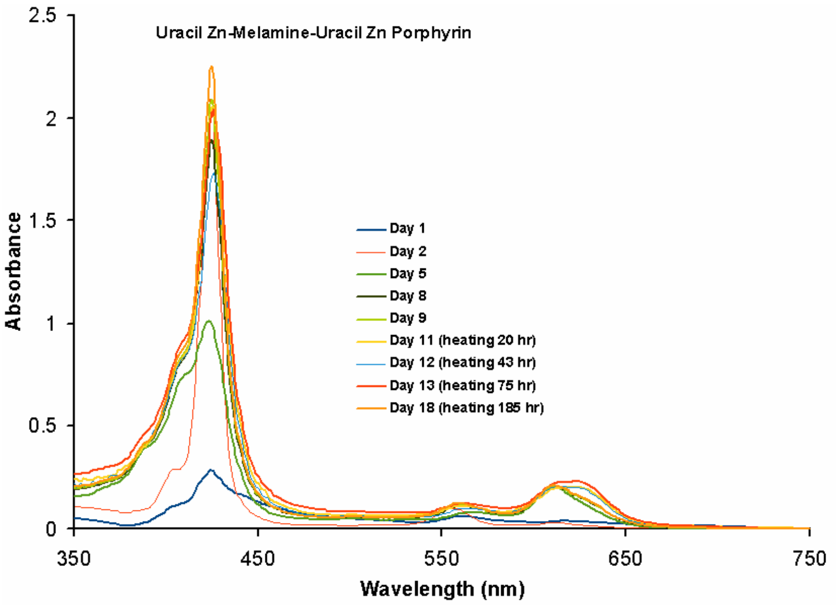
ESI 23: Fluorescence emission spectra of alkylated Zn-Zn (cage **2b-2b**) with melamine in dry THF. The mixture solution was excited at 560 nm where the OD = 0.12 and band pass = 2 nm. The emission spectra intensity increases as the initially formed aggregates evolve into the more soluble cage structure upon heating the sample for couple of days at 45-47 ^{o}C.



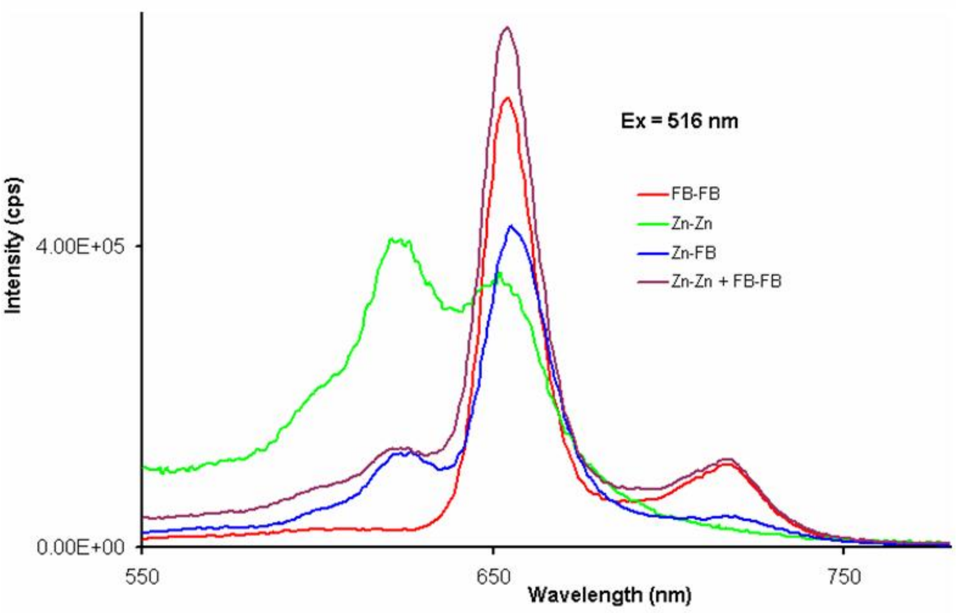
ESI 24: Fluorescence emission spectra of alkylated Zn-FB (cage **2a-2b**) with melamine in dry THF. There is a 1:2:1 mixture of cages containing **2a-2a**, **2a-2b**, and **2b-2b**. Excitation is at 560 nm where the OD = 0.10 and band pass = 2 nm, and **2b** absorbs ~5 times greater than **2a**. The emission spectra intensity increases as the initially formed aggregates evolve into the more soluble cage structure upon heating the sample for couple of days at 45-47 ^{o}C. The relative increase of the zinc complex band with time indicates more of **2b** is in the cage compared to the initially formed aggregates.



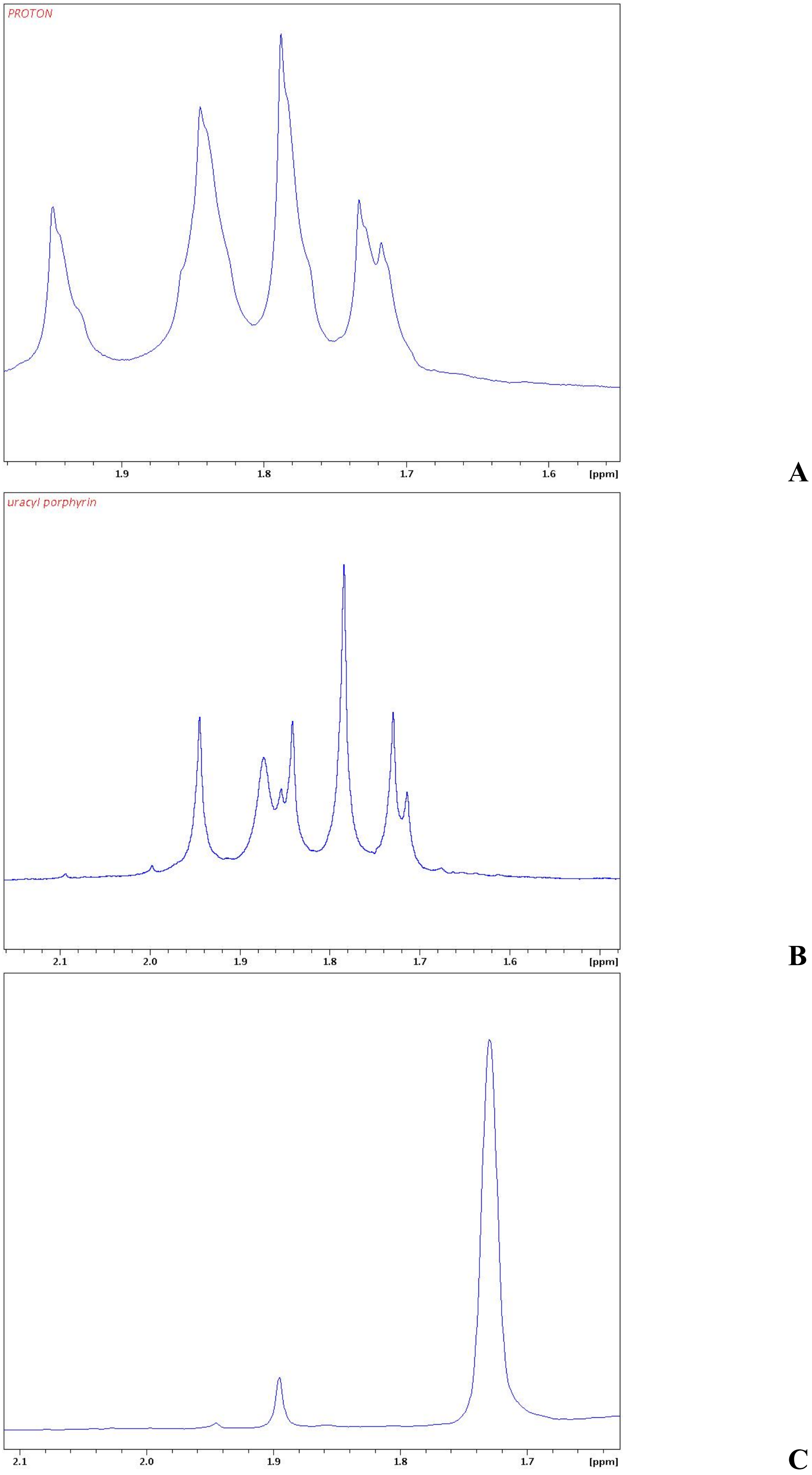
ESI 25: UV-visible spectra of uracil FB-melamine-uracil FB (cage **1a-1a**) in dry THF with heating at 45-47 ^{o}C as indicated. The large background is due to the large number and size distribution of aggregates of the poorly soluble porphyrin. The absorption intensity, e.g. of the Soret band as measured from the background/baseline, increases as **1a** becomes soluble and self-assembles into the cage mediated by H-bonding with the bis(decyl)melamine.



ESI 26: UV-visible spectra of uracil Zn-melamine-uracil Zn (cage **1b-1b**) in dry THF with heating at 45-47 ^{o}C. The poorly soluble porphyrin is highly aggregated. The absorption intensity, e.g. of the Soret band as measured from the background/baseline, increases as **1b** becomes soluble and self-assembles into the cage mediated by H-bonding with the bis(decyl)melamine.

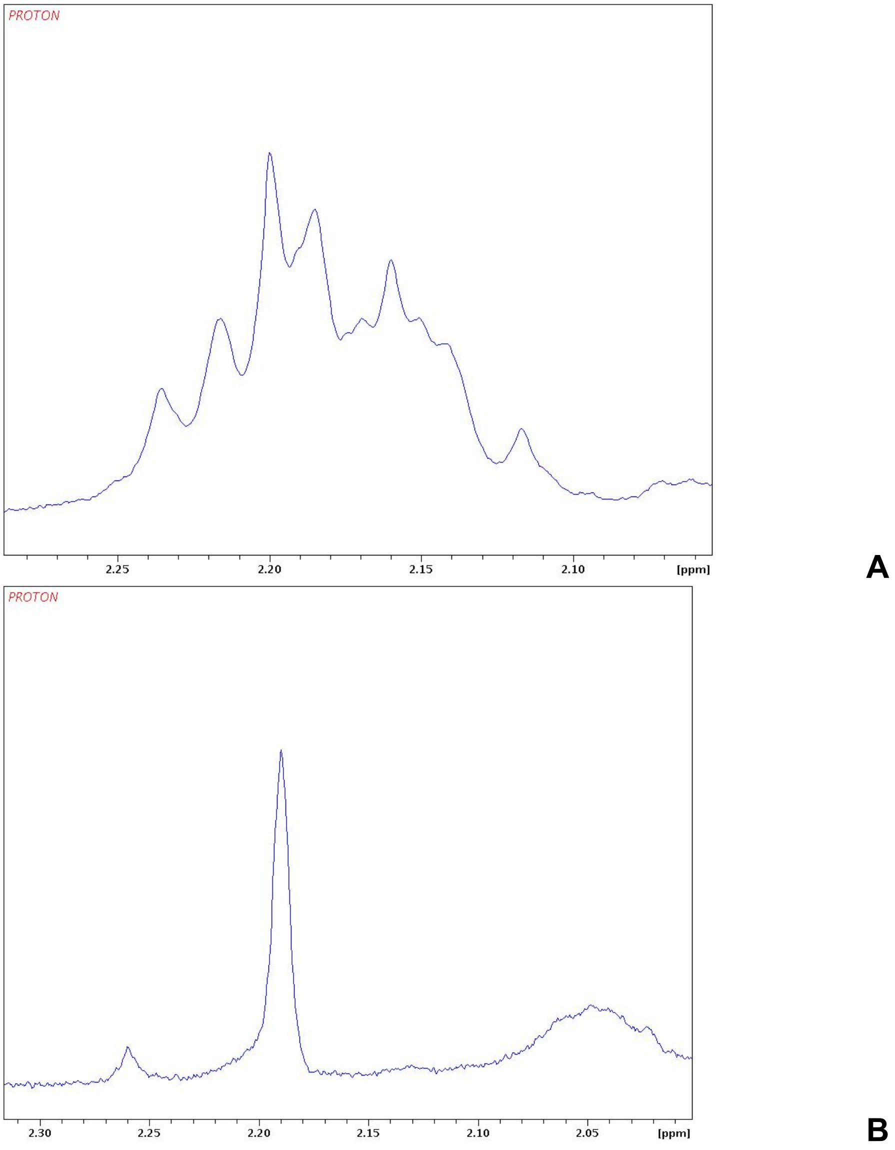


ESI 27: Fluorescence spectra of the cages **1b-1b**, **1a-1a**, and the statistical mixture of **1a-1b** in dry THF with after heating at 45-47 ^{o}C for several days. Excitation is at 516 nm, band pass 2 nm.

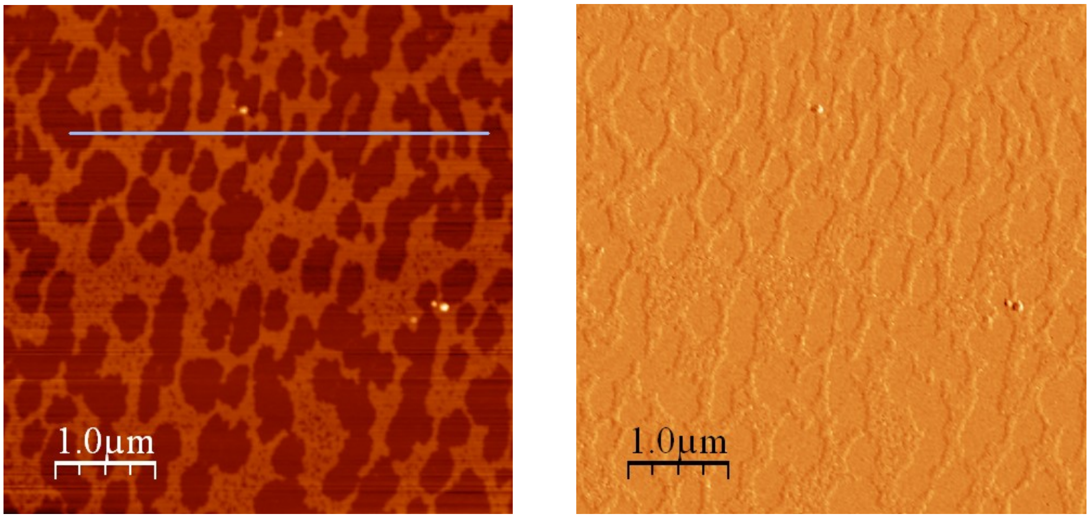


ESI 28. Expansion of ^{1}H NMR of the 6-methyl uracyl resonance for (A) the statistical mixture of atropisomers of porphyrin **1b** after one column purification in DMSO-d_6; (b) **1b** in DMSO-d_6 after complete purification. (c) After formation of the cage, there is only one uracyl methyl resonance at 1.88 ppm in THF-d_8 which is consistent with formation of the α^4 atropisomer. The resonance at 1.74 is the THF solvent.

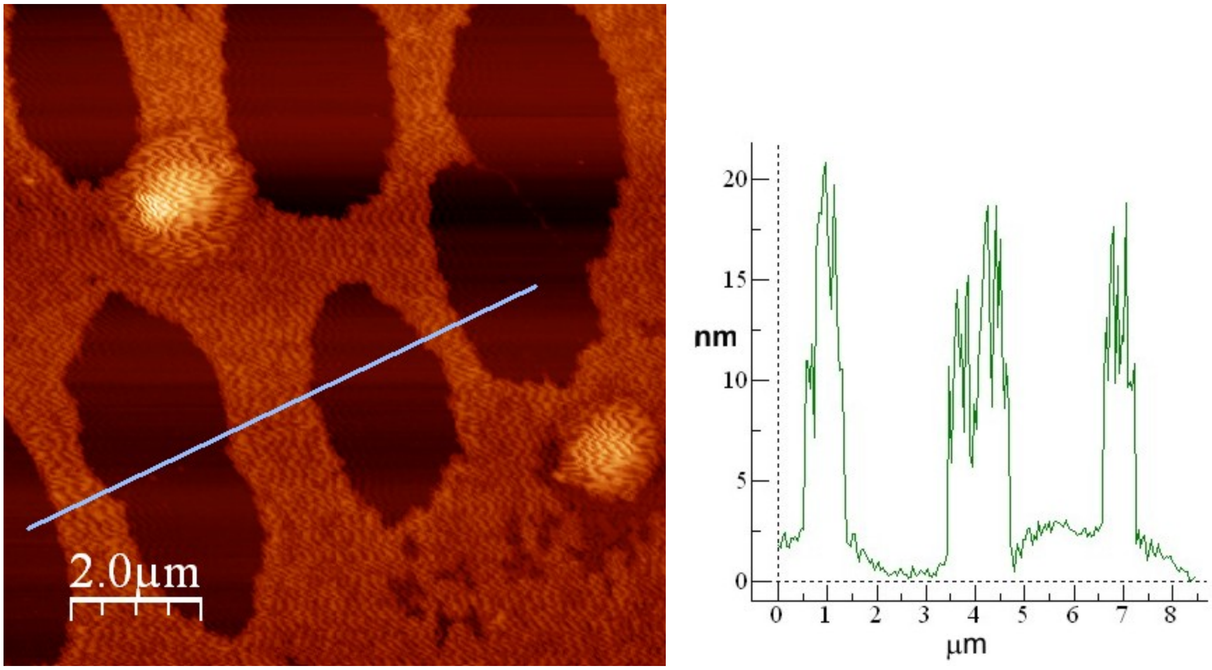
The resonance for the methyl uracyl on the cage in THF-d_8 is shifted by ~0.1 ppm, from where this peak shows up for the non-assembled compounds in DMSO-d_6.[5, 6, 11, 12]



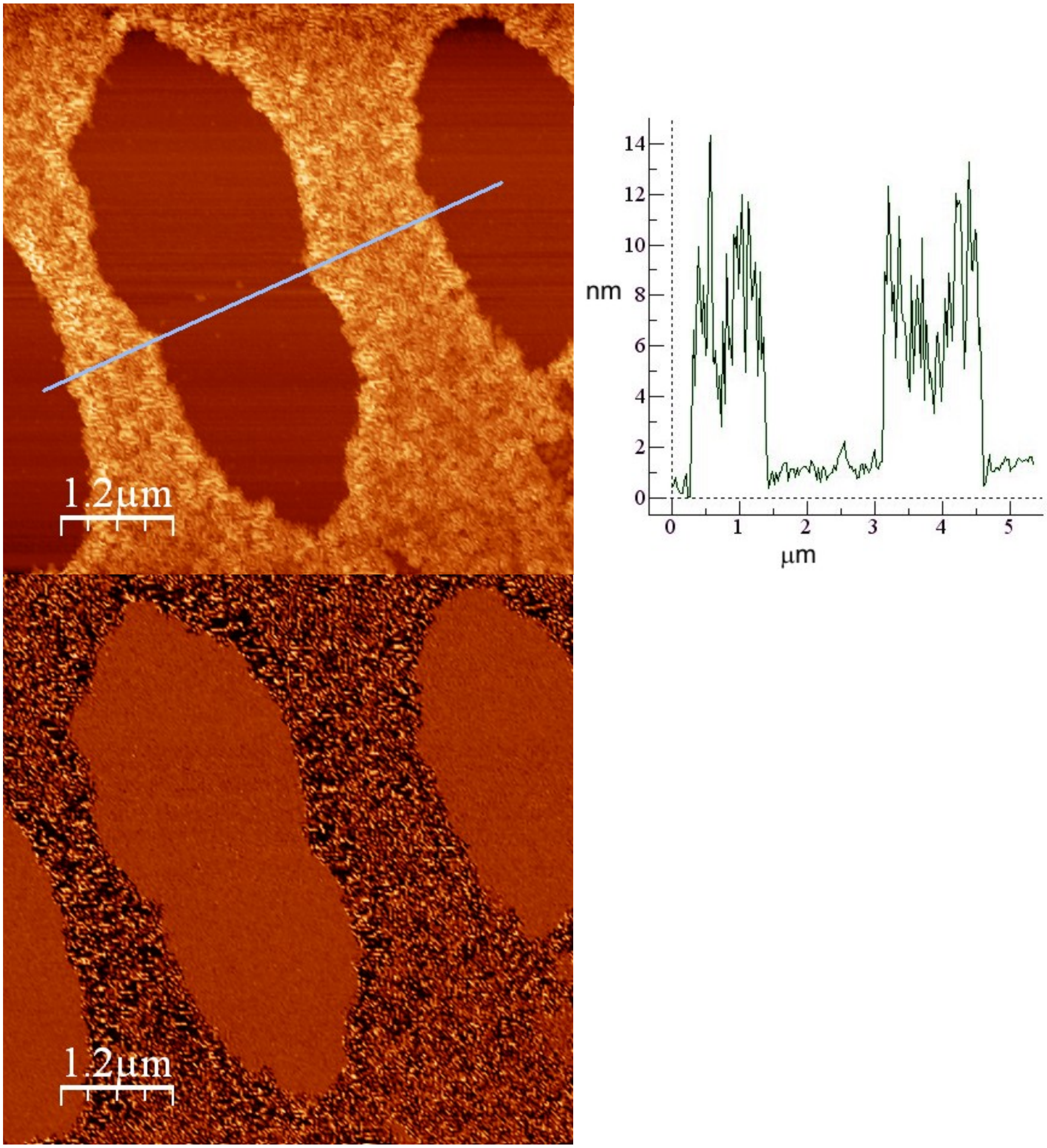
ESI 29. Expansion of ^{1}H NMR of the 6-methyl uracyl resonance for (A) the statistical mixture of atropisomers of porphyrin **2b** in methanol-d_4 after one column purification; (b) After formation of the cage, there is only one uracyl methyl resonance at 2.19 ppm in THF-d_8. Residual solvent at 2.05 ppm.



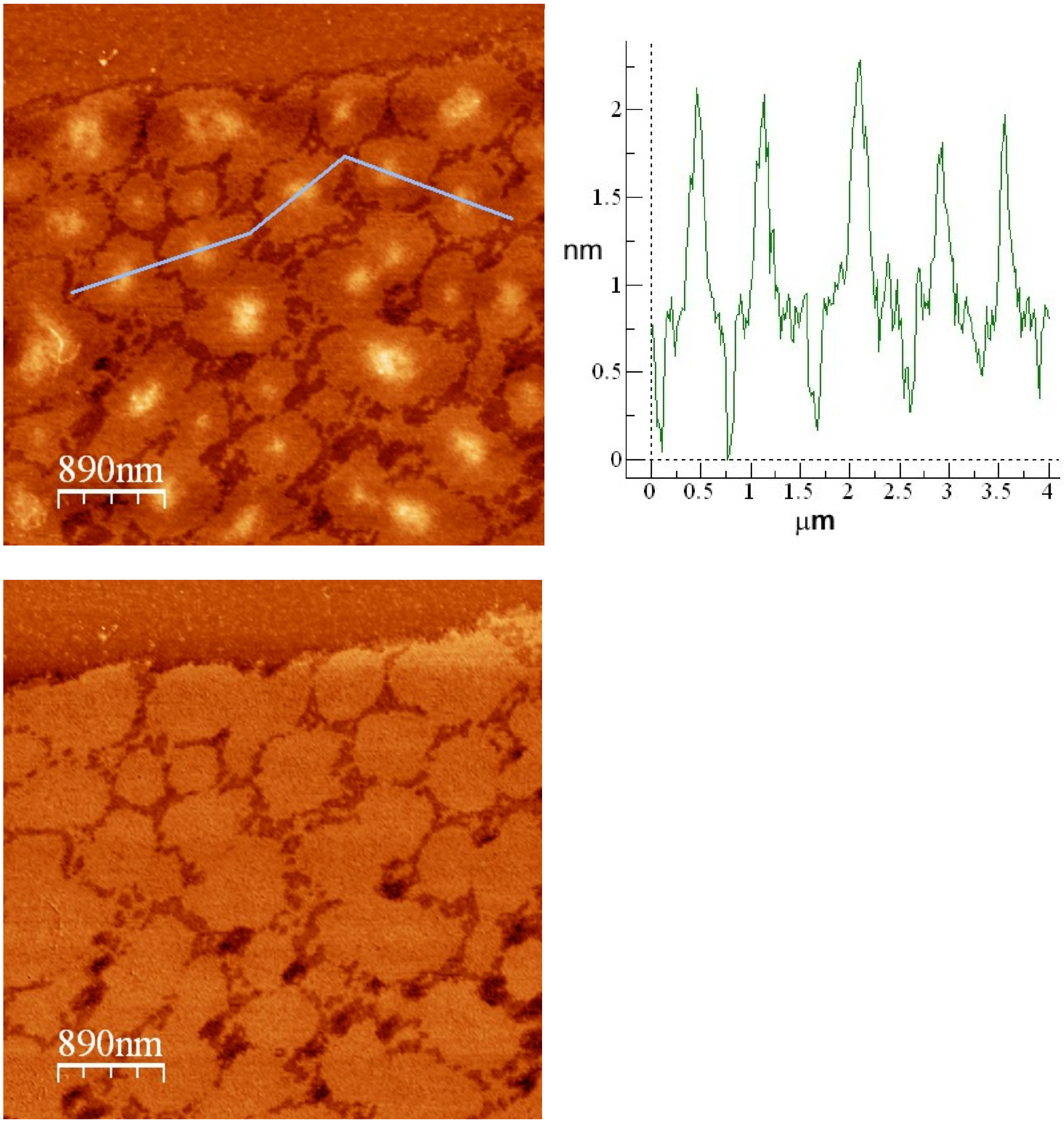
ESI 30. Topology (left) and friction (right) AFM of the cage formed from **2a** using contact mode under ambient conditions. Topography image in the



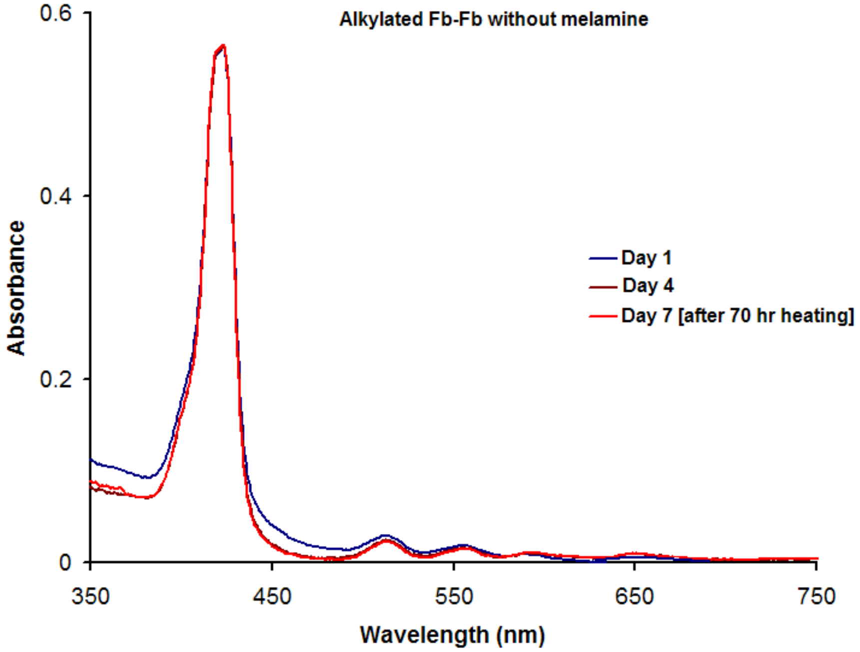
ESI 31. AFM of the cage formed from **2b** using contact mode under ambient conditions. Top: height and height profile, bottom friction.



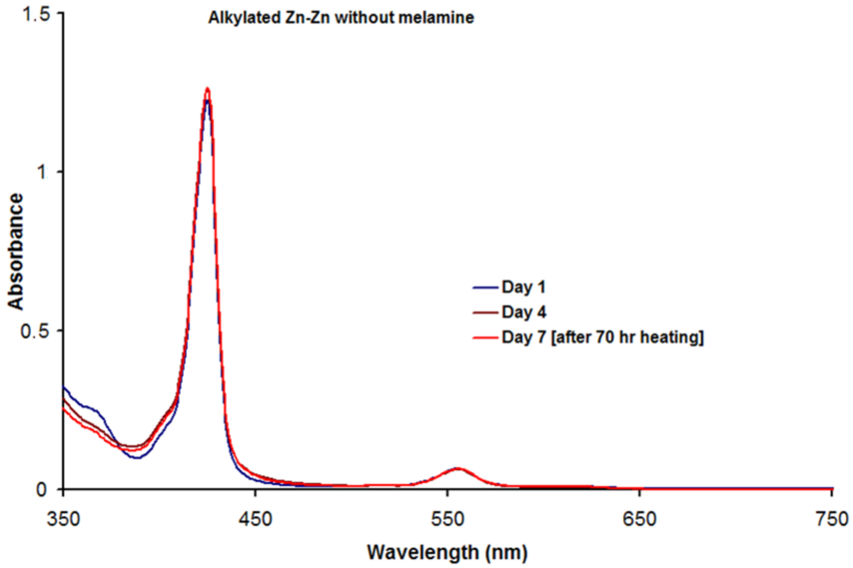
ESI 32. AFM of the cage formed from **2b** using contact mode under ambient conditions. Top: height and height profile, bottom friction.



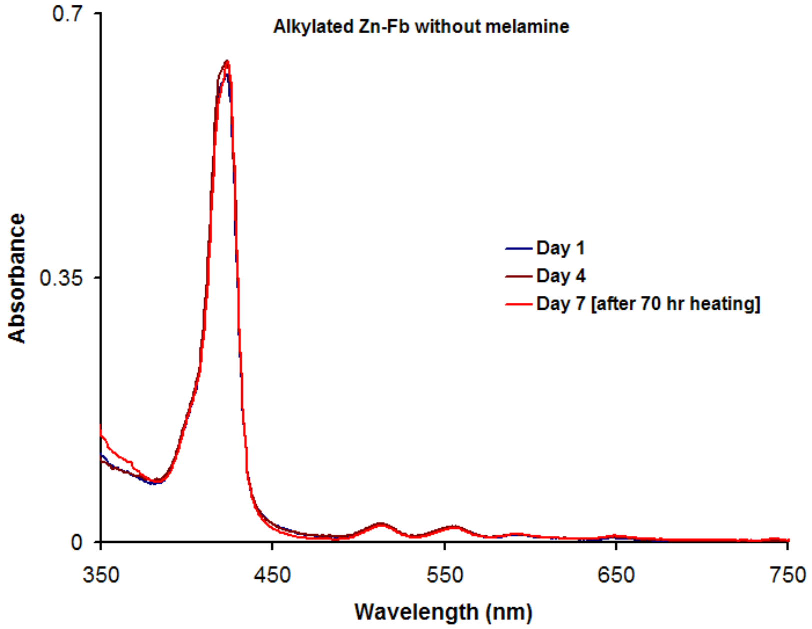
ESI 33. AFM of the 1:2:1 mixture of **2a-2a**, **2a-2b**, **2b2b** cages formed from the mixture of **2a** and **2b** with the bis(decyl)melamine. Contact mode under ambient conditions. Top height and profile, bottom: friction.



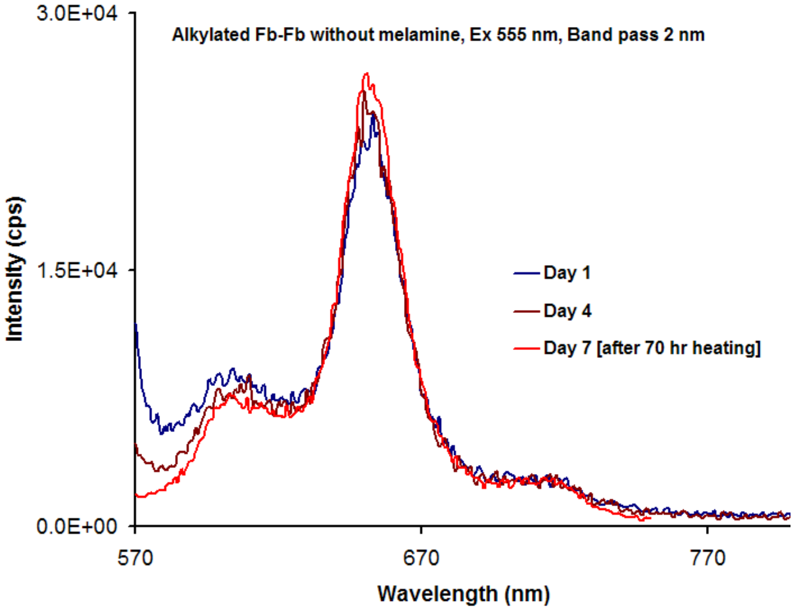
ESI 34. UV-Visible absorption spectra of alkylated FB (**2a**) without melamine in dry THF. The concentration of mixture solution was 12 μM. No change in the absorption intensity was observed at room temperature for four days and then on heating the sample at 45-47 °C for about three days.



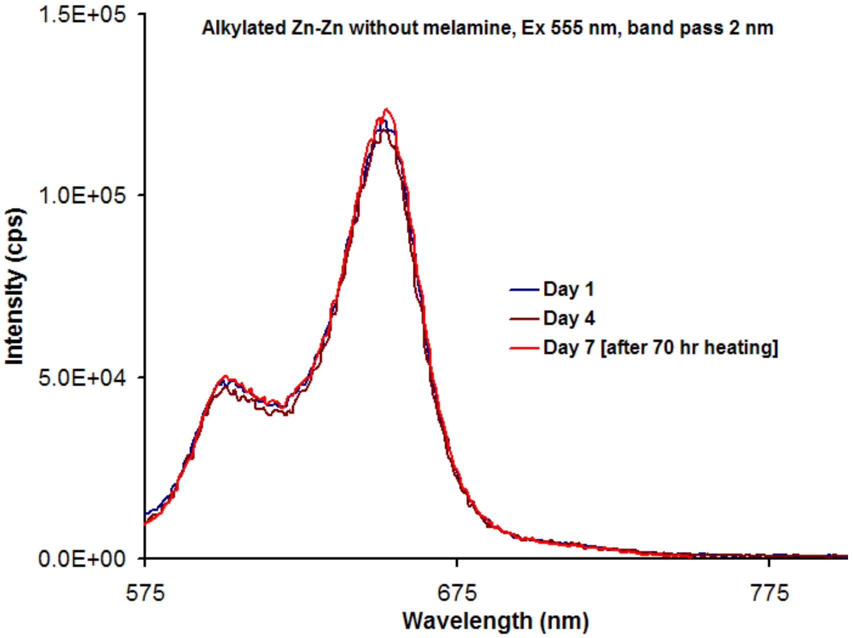
ESI 35. UV-Visible absorption spectra of alkylated Zn (**2b**) without melamine in dry THF. The concentration of mixture solution was 18 μM. No change in the absorption intensity was observed at room temperature for four days and then on heating the sample at 45-47 °C for about three days.



ESI 36. UV-Visible absorption spectra of alkylated Zn and FB (**2a** and **2b**) without melamine in dry THF. The concentration of mixture solution was 14 μM. No ch and ange in the absorption intensity was observed at room temperature for four days and then on heating the sample at 45-47 °C for about three days.



ESI 37. Emission spectra of alkylated FB (**2a**) without melamine in dry THF. The mixture solution was excited at 555 nm where the OD = 0.014 and band pass = 2 nm. No change in the emission intensity was observed at room temperature for four days and then on heating the sample at 45-47 °C for about three days.



ESI 38. Emission spectra of alkylated Zn (**2b**) without melamine in dry THF. The mixture solution was excited at 555 nm where the OD = 0.13 and band pass = 2 nm. No change in the emission intensity was observed at room temperature for four days and then on heating the sample at 45-47 ^{o}C for about three days.

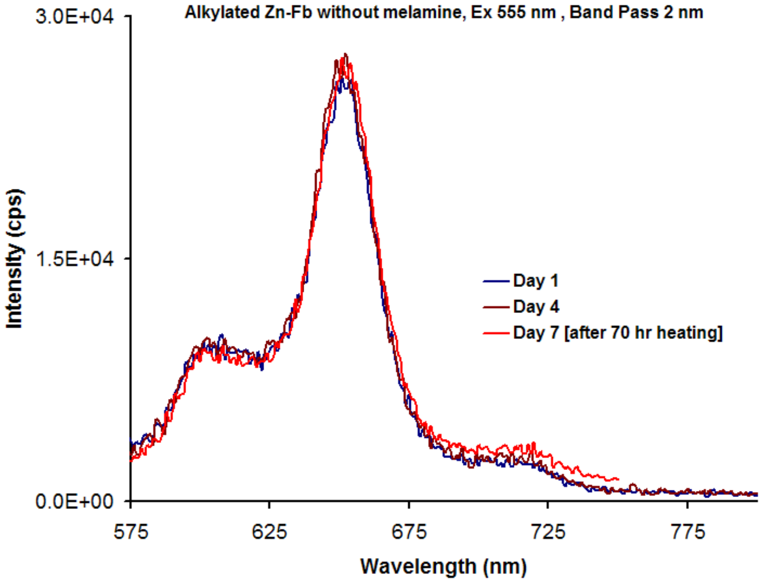


Fig 39. Emission spectra of alkylated Zn and FB (**2a** and **2b**) without melamine in dry THF. The mixture solution was excited at 555 nm where the OD = 0.017 and band pass = 2 nm. No change in the emission intensity was observed at room temperature for four days and then on heating the sample at 45-47 ^{o}C for about three days.

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