

Electronic Supplementary Information for:

^2H NMR Reveals Liquid State-Like Dynamics of Arene Guests Inside Hexameric Pyrogallol[4]arene Capsules in the Solid State.

Irazema J. Islas,^{†a} Dillan Stengel,^{†a} Cesar A. Garcia,^a J. Bennett Addison,^a George N. Samaan,^a Gregory P. Holland,^a and Byron W. Purse^{*a,b}

^a Department of Chemistry and Biochemistry and ^b the Viral Information Institute, San Diego State University, San Diego, CA 92129, USA. E-mail: bpurse@sdsu.edu

Table of Contents

1. Additional molecular models for encapsulated fluorene, fluoranthene, and pyrene	S2-S3
2. Static solid-state ^2H NMR Spectra of fluorene- d_2 encapsulated in 1a ₆	S3
3. Static solid-state ^2H NMR Spectra of fluoranthene- d_{10} encapsulated in 1a ₆	S4
4. Static solid-state ^2H NMR Spectra of pyrene- d_{10} encapsulated in 1a ₆	S5
5. Static solid-state ^2H NMR Spectra of fluorene- d_2 encapsulated in 1b ₆	S6
6. Static solid-state ^2H NMR Spectra of fluoranthene- d_{10} encapsulated in 1b ₆	S6
7. Static solid-state ^2H NMR Spectra of pyrene- d_{10} encapsulated in 1b ₆	S7
8. Static solid-state ^2H NMR spectra of guests fluorene- d_2 , fluoranthene- d_{10} , and pyrene- d_{10}	S8
9. Static solid-state ^2H NMR Spectra of 5 α -2,4-($^2\text{H}_4$)-cholestan-3-one	S8
10. Differential scanning calorimetry of fluorene, fluoranthene, and pyrene each milled with either 1a or 1b pyrogallol[4]arene	S9
11. ^1H NMR Spectra of 1a ₆ in CDCl_3 alone, or with fluorene, fluoranthene, or pyrene as guest	S10
12. ^1H NMR Spectra of 1b ₆ in CDCl_3 alone, or with fluorene, fluoranthene, or pyrene as guest	S10
13. X-ray powder diffraction spectra	S11
14. General Experimental and Synthetic Details	S13
15. References	S15

All molecular models were prepared in Spartan '08. Geometry minimizations were performed by fixing the atoms of the hexamer as determined from an X-ray crystal structure¹ and minimizing the guests on the interior at the AM1 level of theory. Alkyl groups have been truncated from the models for clarity.

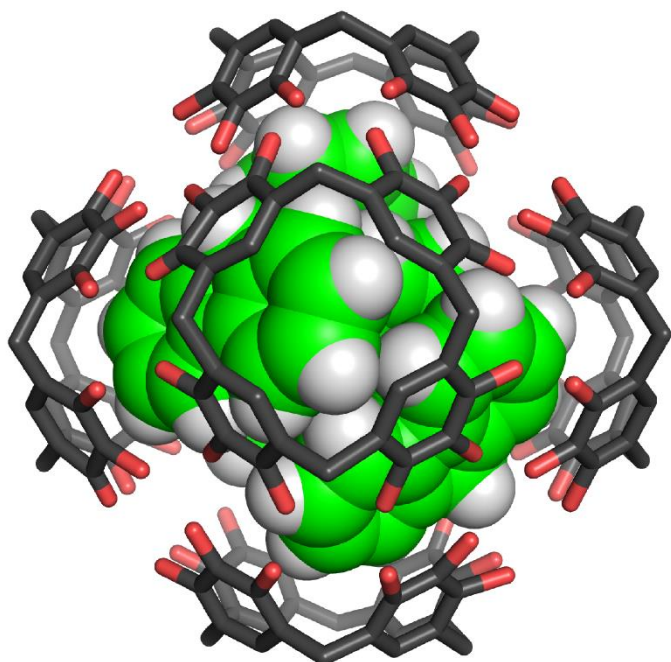


Figure S1. Molecular model for encapsulated fluorene in **16**.

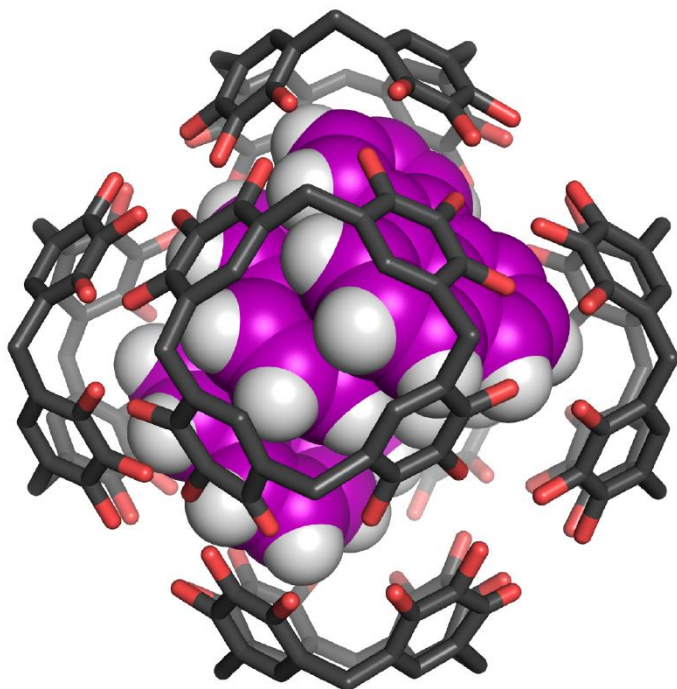


Figure S2. Molecular model for encapsulated fluoranthene in **16**.

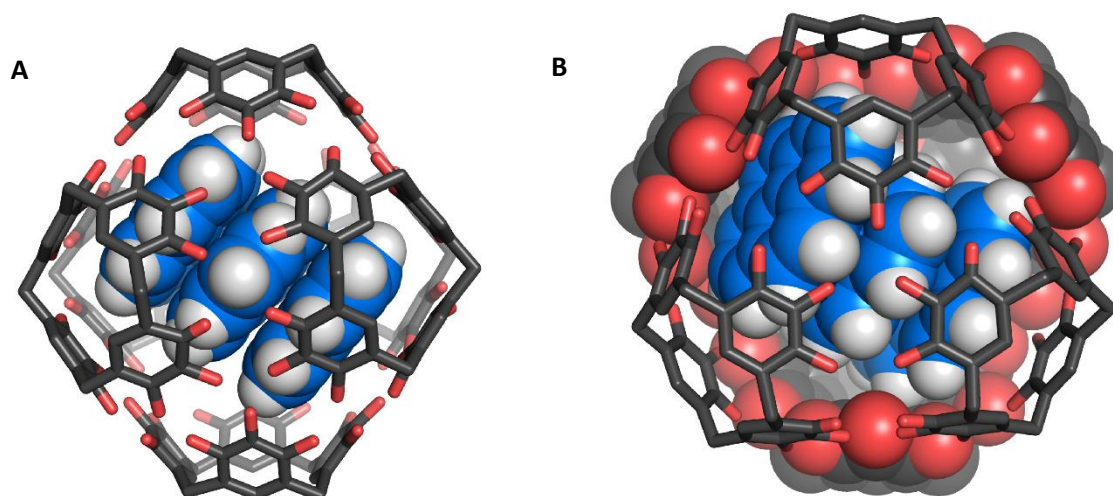


Figure S3. **A**, Molecular model for encapsulated pyrene in **16**. **B**, Space-filling version of **A**, rotated, showing tightness of guest fit.

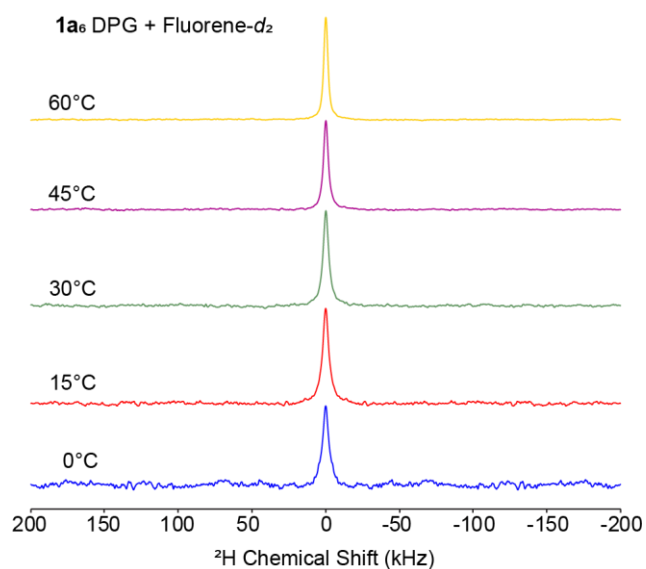


Figure S4. Static solid-state ^2H NMR spectra of **1a₆** decyl pyrogallol[4]arene-encapsulated fluorene- d_2 between 0°C and 60°C . The maximum intensity of the 0°C to 45°C spectra were scaled to the same height as the 60°C spectra. The spectra at lower temperature have less signal intensity when normalized using the same number of scans (8192) and the same vertical display (not shown).

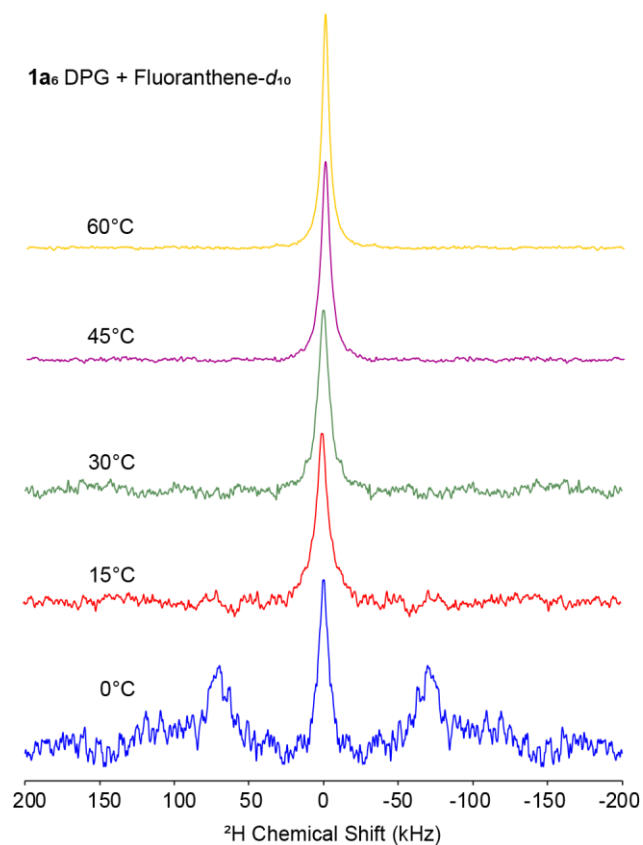


Figure S5. Static solid-state ^2H NMR spectra of **1a₆** decyl pyrogallol[4]arene-encapsulated fluoranthene- d_{10} between 0°C and 60°C. The maximum intensity of the 0°C to 45°C spectra were scaled to the same height as the 60°C spectra. The spectra at lower temperature have less signal intensity when normalized using the same number of scans (8192) and the same vertical display (not shown).

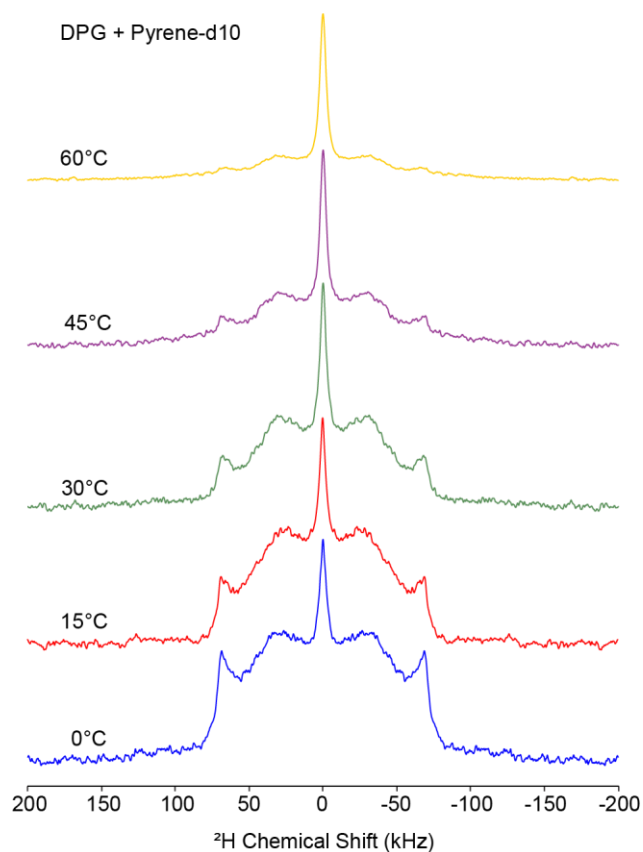


Figure S6. Static solid-state ^2H NMR spectra of **1a₆** decyl pyrogallol[4]arene-encapsulated pyrene- d_{10} between 0°C and 60°C. The maximum intensity of the 0°C to 45°C spectra were scaled to the same height as the 60°C spectra. The spectra at lower temperature have less signal intensity when normalized using the same number of scans (8192) and the same vertical display (not shown).

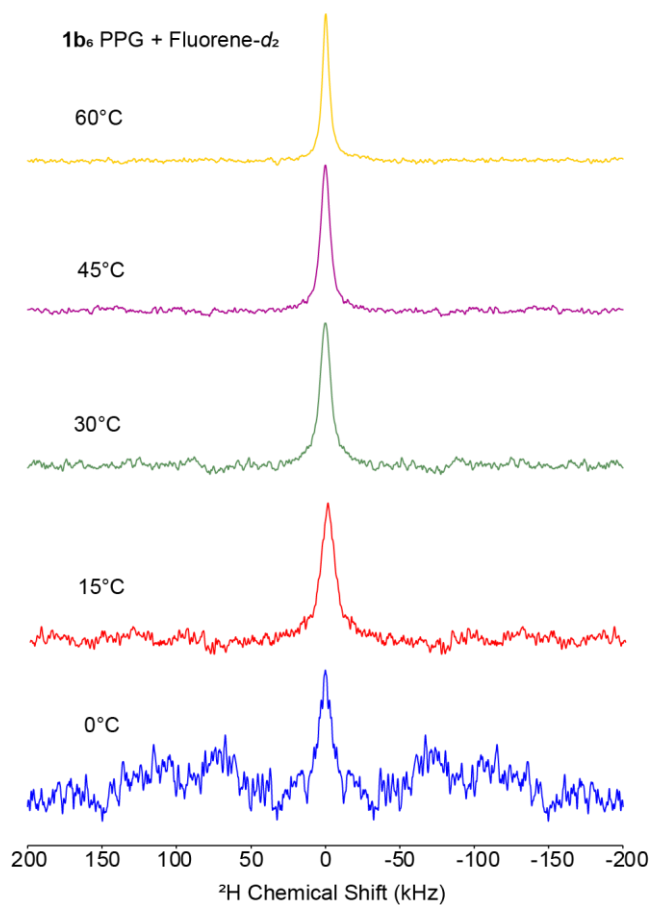


Figure S7. Static solid-state ²H NMR spectra of **1b₆** propyl pyrogallol[4]arene-encapsulated fluorene-*d*₂ between 0°C and 60°C. The maximum intensity of the 0°C to 45°C spectra were scaled to the same height as the 60°C spectra. The spectra at lower temperature have less signal intensity when normalized using the same number of scans (8192) and the same vertical display (not shown).

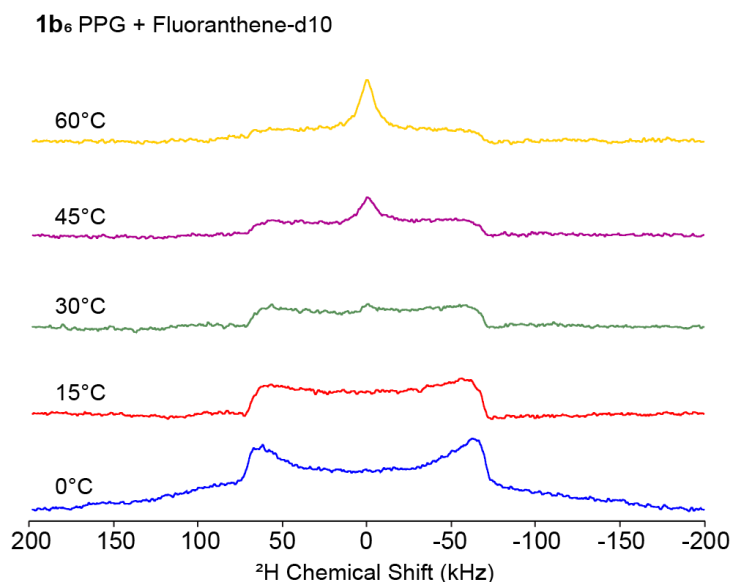


Figure S8. Static solid-state ²H NMR spectra of **1b₆** propyl pyrogallol[4]arene-encapsulated fluoranthene- *d*₁₀ between 0°C and 60°C. The maximum intensity of the 0°C to 45°C spectra were scaled to the same height as the 60°C spectra.

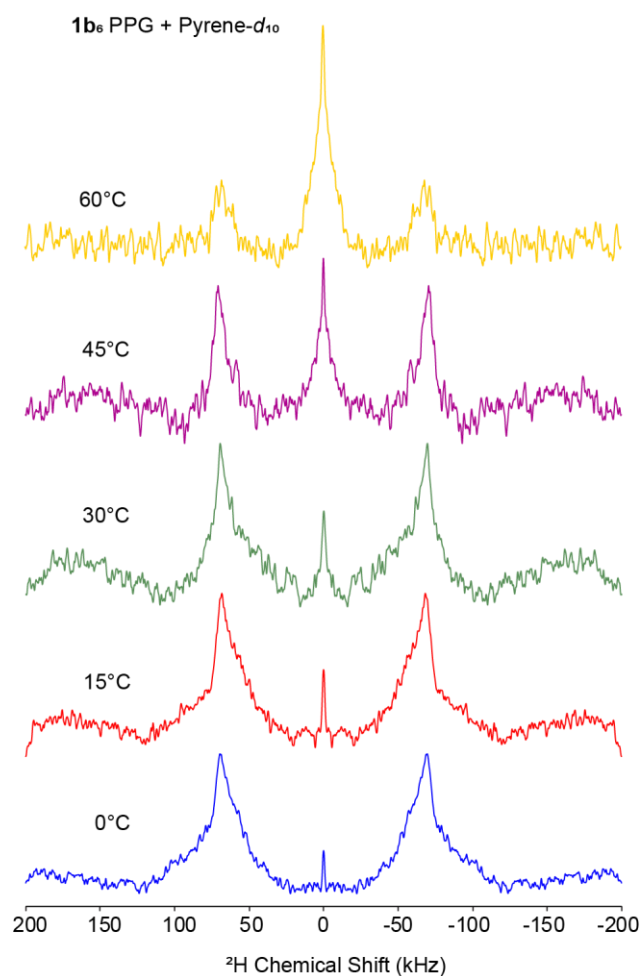


Figure S9. Static solid-state ^2H NMR spectra of 1b_6 propyl pyrogallol[4]arene-encapsulated pyrene- d_{10} between 0°C and 60°C. The maximum intensity of the 0°C to 45°C spectra were scaled to the same height as the 60°C spectra.

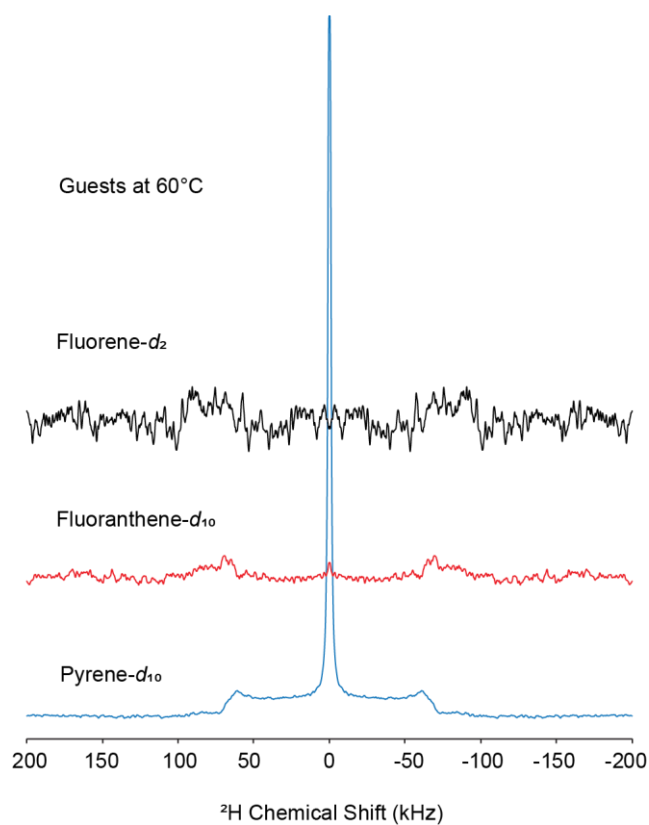


Figure S10. Static solid-state ^2H NMR spectra of guests fluorene- d_2 , fluoranthene- d_{10} , and pyrene- d_{10} at 60°C. Each spectra is scaled differently to show their most prominent features.

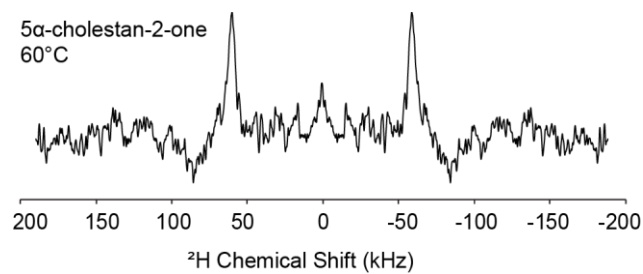


Figure S11. Static solid-state ^2H NMR spectra of 5 α -2,4-($^2\text{H}_4$)-cholestan-3-one at 60°C.

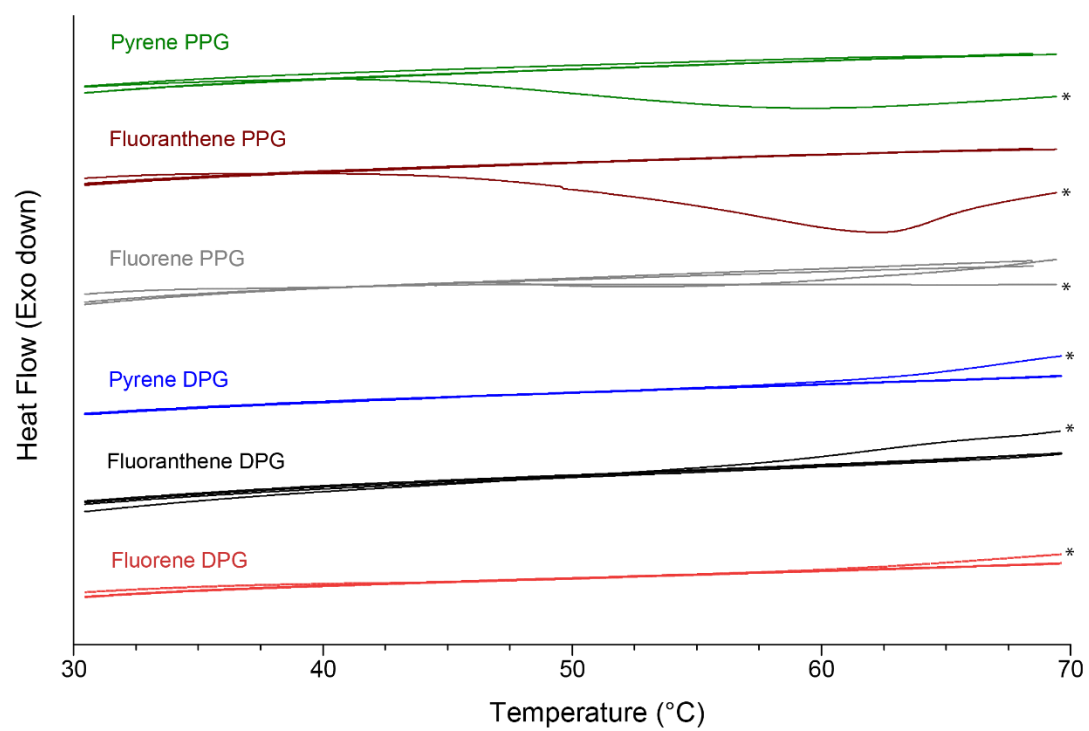


Figure S12. Differential scanning calorimetry of fluorene, fluoranthene, and pyrene each milled with either **1a₆** (DPG) or **1b₆** (PPG). The asterisks indicate the first heating cycle.

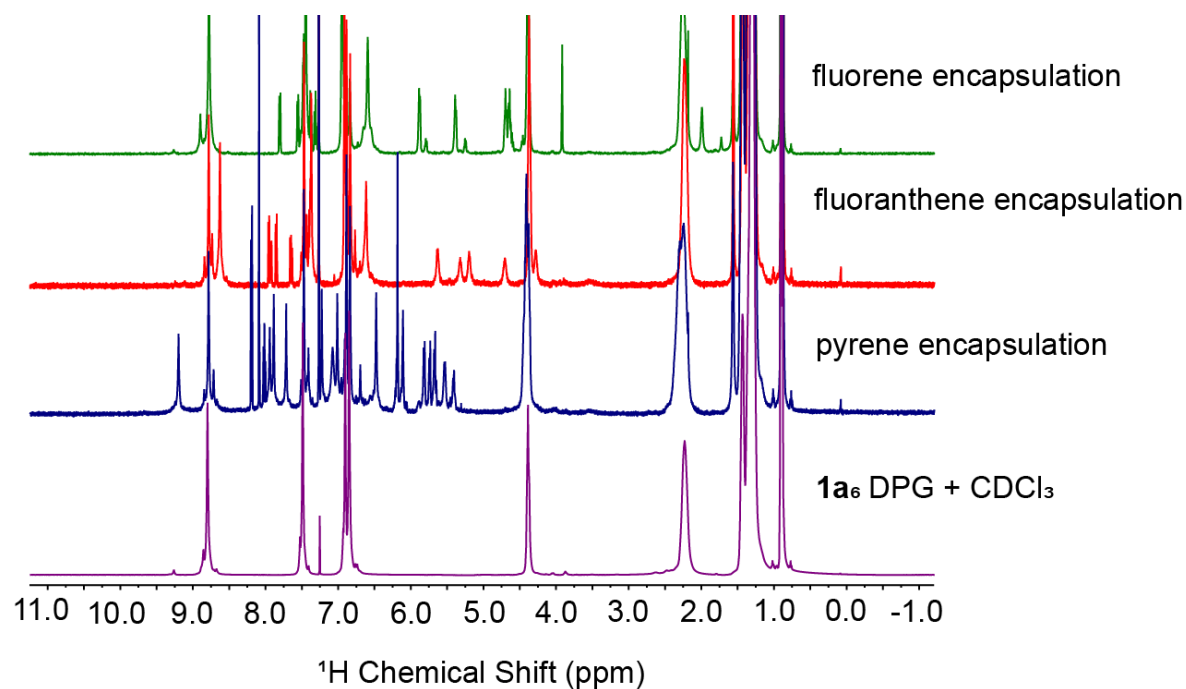


Figure S13. Solution ^1H NMR spectra of decyl pyrogallol[4]arene (DPG) 1a_6 in CDCl_3 and with encapsulated fluorene, fluoranthene, or pyrene. (500 MHz; 298 K)

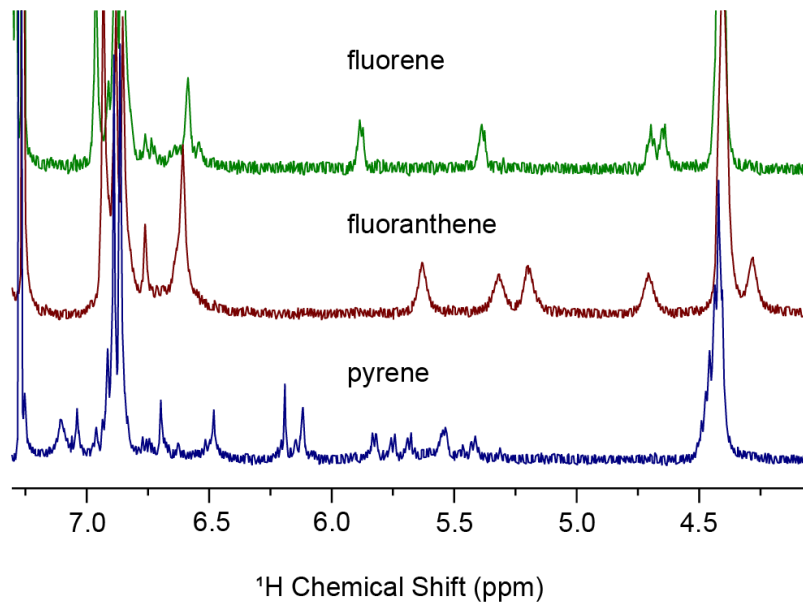


Figure S14. Solution ^1H NMR spectra of propyl pyrogallol[4]arene (PPG) 1b_6 in CDCl_3 with encapsulated fluorene, fluoranthene, or pyrene. (500 MHz; 298 K)

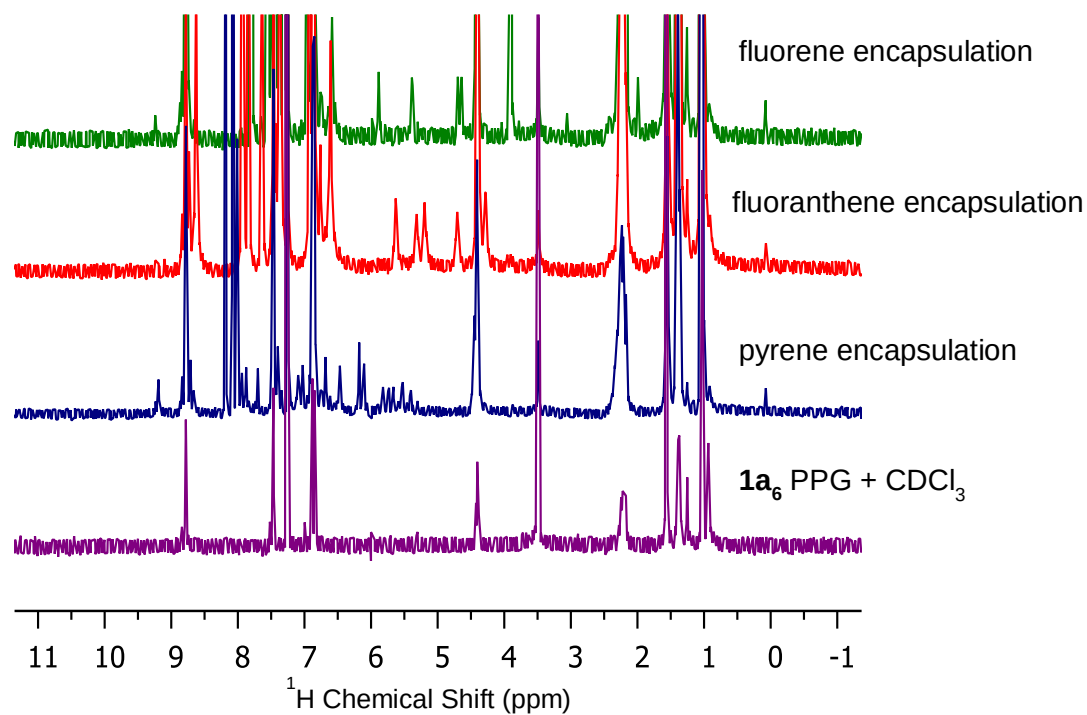


Figure S15 .Solution ¹H NMR spectra of propyl pyrogallol[4]arene (PPG) **1b₆** in CDCl₃ with encapsulated fluorene, fluoranthene, or pyrene. (500 MHz; 298 K)

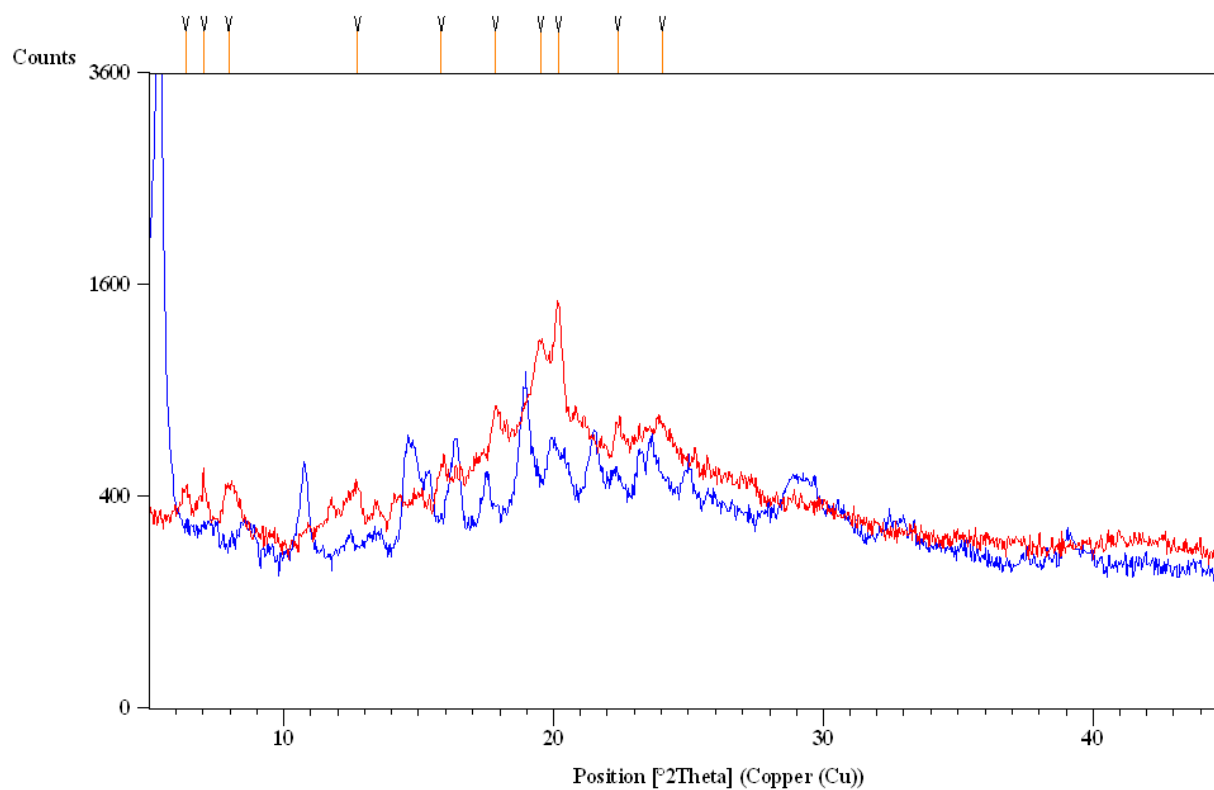


Figure S16. Powder x-ray diffraction spectra of **1a₆** (red) and **1b₆** (blue) with encapsulated fluoranthene.

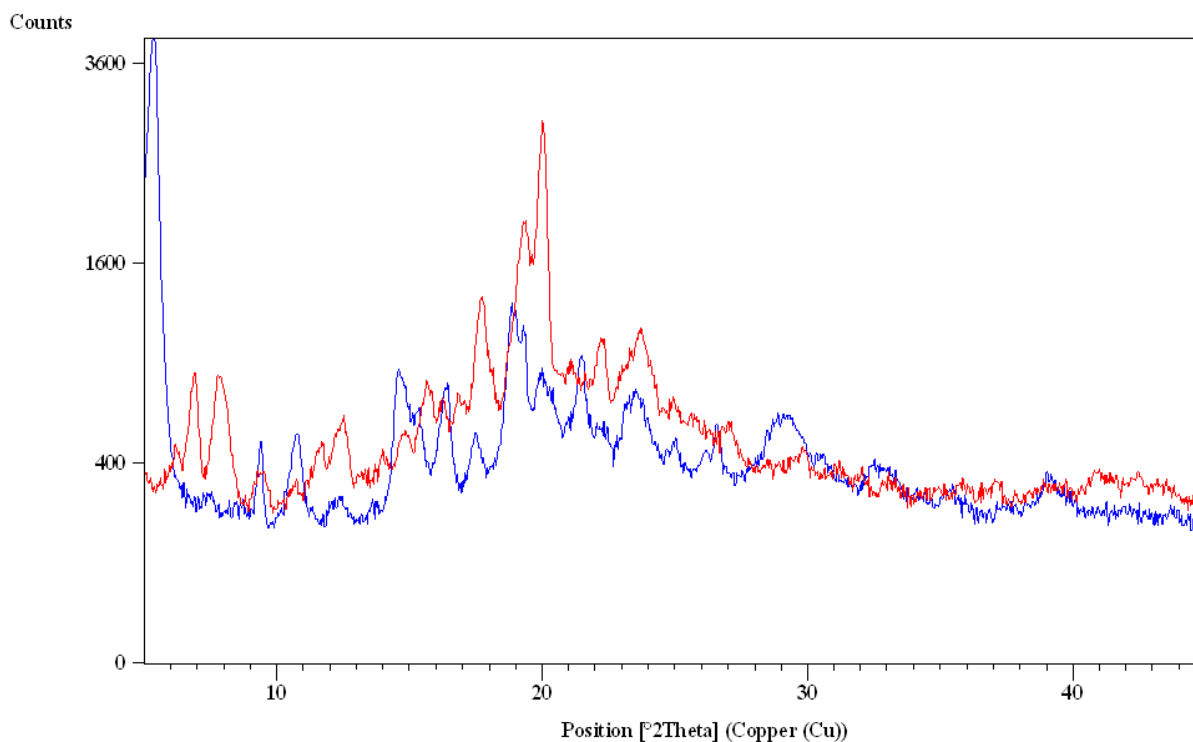
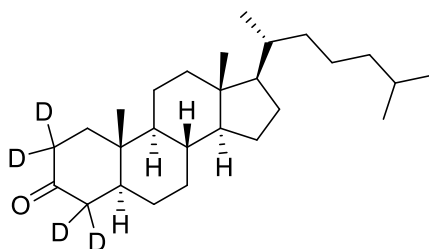


Figure S17. Powder x-ray diffraction spectra of **1a₆** (red) and **1b₆** (blue) with encapsulated fluorene

All powder X-Ray diffraction experiments were acquired on a Panalytical XPert PRO diffractometer using Cu K X-ray tube radiation and a voltage of 45 kV and 40 mA. The diffraction pattern was scanned over the angular range of 5–45° with a step size of 0.04° and the sample was held at room temperature (296 K).

General Experimental

All manipulations were carried out under a nitrogen atmosphere. All glassware was oven dried immediately prior to use. All reagents, guests, and solvents were obtained from commercial sources and used without further purification, with the following exceptions. Solution ^1H NMR spectra were acquired on Varian 400 MHz, Varian 500 MHz, and Bruker 600 MHz NMR spectrometers and recorded at 298 K. Chemical shifts are referenced to the residual solvent peaks and given in parts per million (ppm). Deuterated NMR solvents and deuterated guests, except for fluorene- d_2 , were purchased from Cambridge Isotope Laboratories. Pyrogallol[4]arenes were synthesized as previously reported.^{2,3} 5α -2,4-($^2\text{H}_4$)-cholestan-3-one and fluorene- d_2 were synthesized as described below using commercial starting materials.



5α -2,4-($^2\text{H}_4$)-cholestan-3-one. 5α -cholestan-3-one (300 mg, 0.77 mmol) is suspended in D_2O (1.5 ml) and dry dioxane (1.5 ml) then sodium metal (178 mg, 7.7 mmol) is added and the reaction heated to 90°C for 3 hours. The reaction is monitored by MS until a mass increase of > 3 amu is observed, indicating the replacement of, on average, at least three protons with deuterons. The reaction is cooled to 0°C , and the product extracted with diethyl ether and the solvent is evaporated to give white product, which had, on average, 75% substitution of deuterium for the four hydrogen atoms α to the carbonyl (285 mg, 95% yield). MS (APCI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{43}\text{DO}$ 391.6; Found 390.5

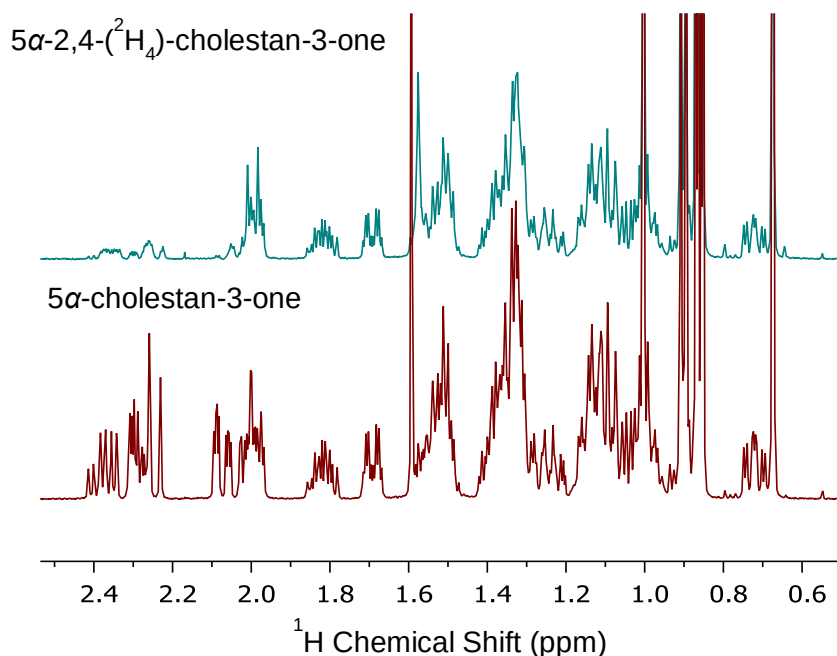
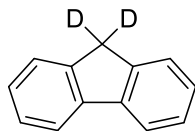


Figure S18. Solution ^1H NMR of 5α -cholestan-3-one and 5α -2,4-($^2\text{H}_4$)-cholestan-3-one. The intensity of the peaks between 2.45 and 2.05 are reduced in the 5α -2,4-($^2\text{H}_4$)-cholestan-3-one compared to 5α -cholestan-3-one. (500 MHz; 298 K)



Fluorene-*d*₂.⁴ 1.65g (9.93 mmol) of fluorene was dissolved in 10 mL DMSO-*d*₆ under N₂. Then 1.2 g (50 mmol) of NaH was added at 23 °C and stirred for 2 hours. The reaction was quenched with D₂O, the solid product was collected by filtration, and washed with H₂O. The product was then purified by flash chromatography using a hexane to ethyl acetate gradient to yield the desired product, a white crystalline powder. ¹H NMR (500 MHz, CDCl₃): δ 7.78 (1H, dd) δ 7.54 (1H, dd) δ 7.37 (1H, t) δ 7.30 (1H, t). MS (APCI) m/z: [M + H]⁺ Calcd for C₁₃H₉D₂ 169.2; Found 169.1

References

- (1) Dalgarno, S. J.; Antesberger, J.; McKinlay, R. M.; Atwood, J. L. Water as a Building Block in Solid-State Acetonitrile–Pyrogallol[4]Arene Assemblies: Structural Investigations. *Chem. - A Eur. J.* **2007**, *13*, 8248–8255.
- (2) Kvasnica, M.; Chapin, J. C.; Purse, B. W. Efficient Loading and Kinetic Trapping of Hexameric Pyrogallolarene Capsules in Solution. *Angew. Chem. Int. Ed.* **2011**, *50*, 2244–2248.
- (3) Gerkenmeier, T.; Iwanek, W.; Avena, C.; Fröhlich, R.; Kotila, S.; Näther, C.; Mattay, J. Self-Assembly of 2,8,14,20-Tetraisobutyl-5,11,17,23-Tetrahydroxyresor[4]Arene. *European J. Org. Chem.* **1999**, 2257–2262.
- (4) Gao, H.; Groves, J. T. Fast Hydrogen Atom Abstraction by a Hydroxo Iron(III) Porphyrine. *J. Am. Chem. Soc.* **2017**, *139*, 3938–3941.