Electronic Supplementary Information

Hierarchical Self-assembly of Amphiphilic Calix[6]arene Wheels and Viologen Axles in Water

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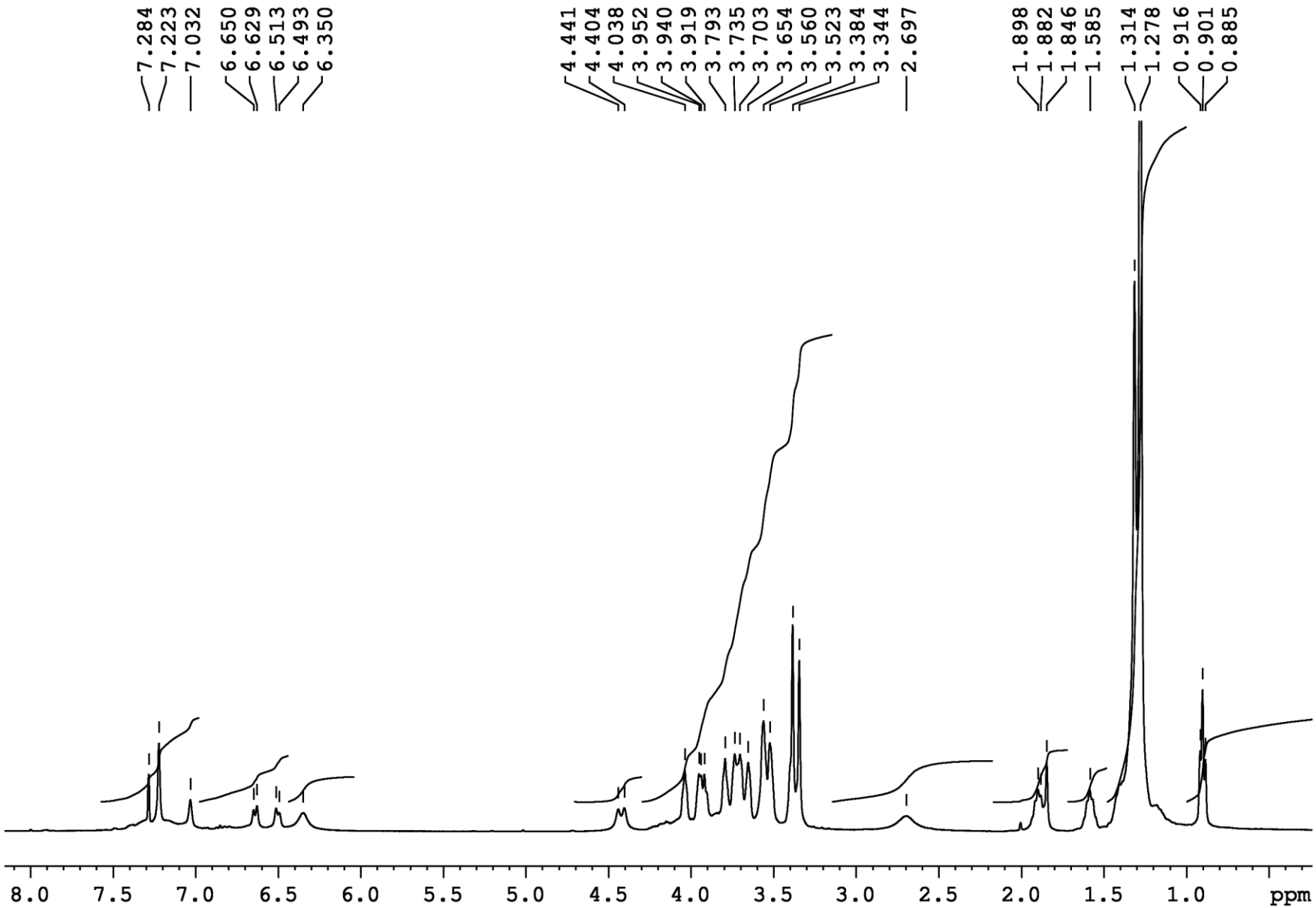


Figure S-1. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of calix[6]arene **CA18**

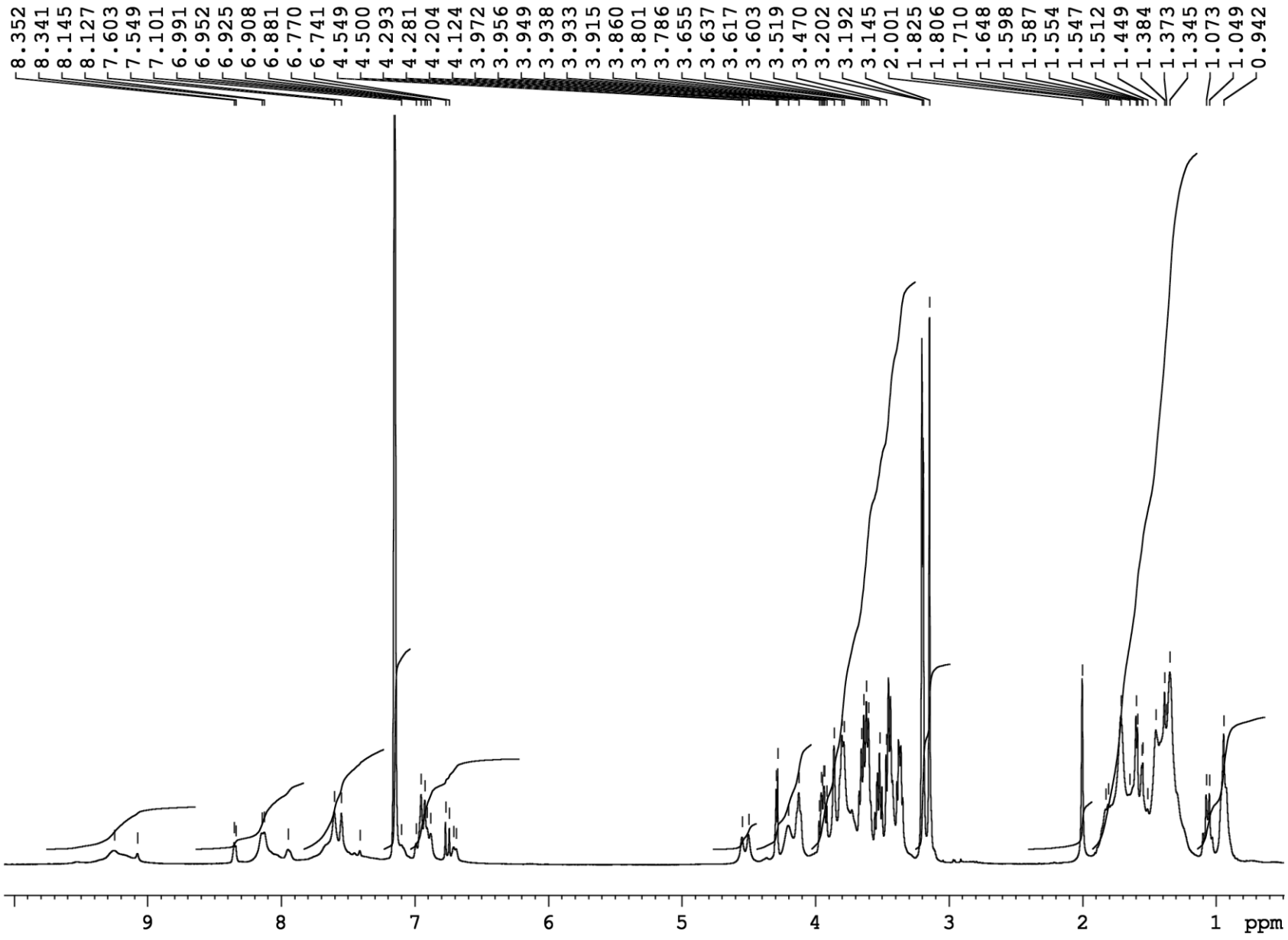


Figure S-2. ^{1}H NMR spectra (300 MHz, C_6D_6) of pseudorotaxane **P**[**CA8⊃DOV**]

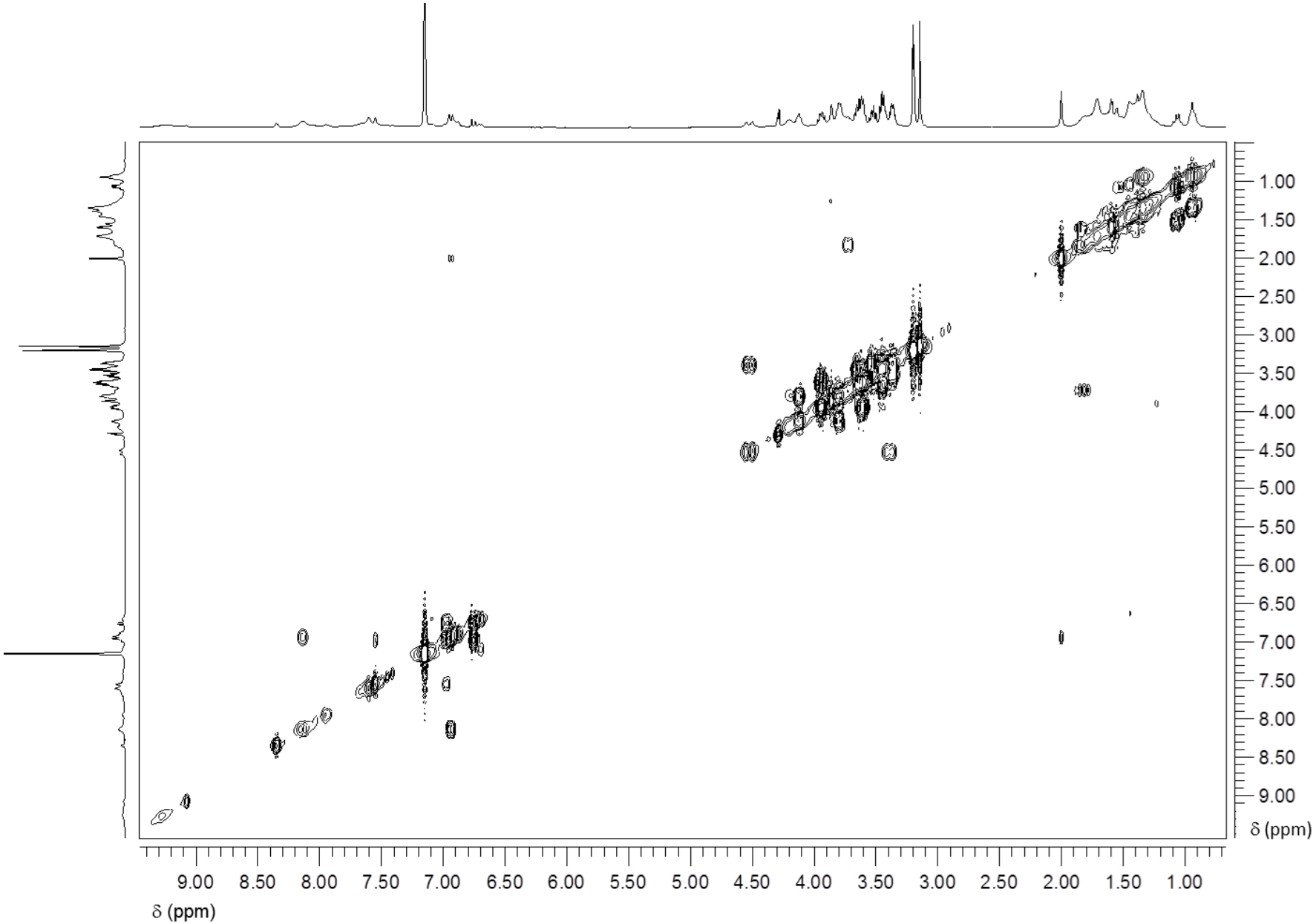


Figure S-3. 2D COSY NMR spectra (300 MHz, C_6D_6) of pseudorotaxane **P**[**CA8⊃DOV**]

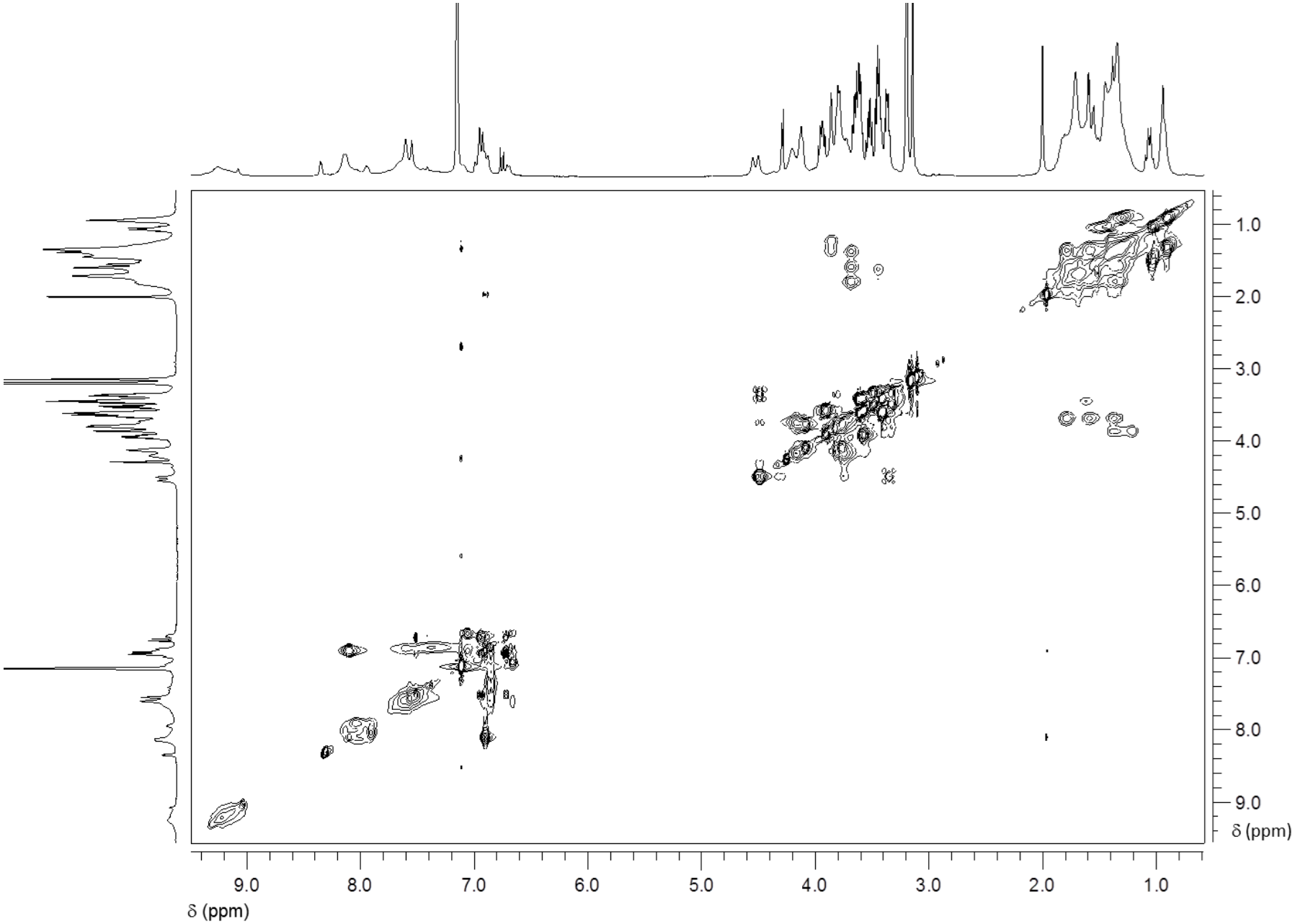


Figure S-4. 2D TOCSY NMR spectra (300 MHz, C_6D_6, mixing time = 0.06 s) of pseudorotaxane **P**[**CA8⊃DOV**]

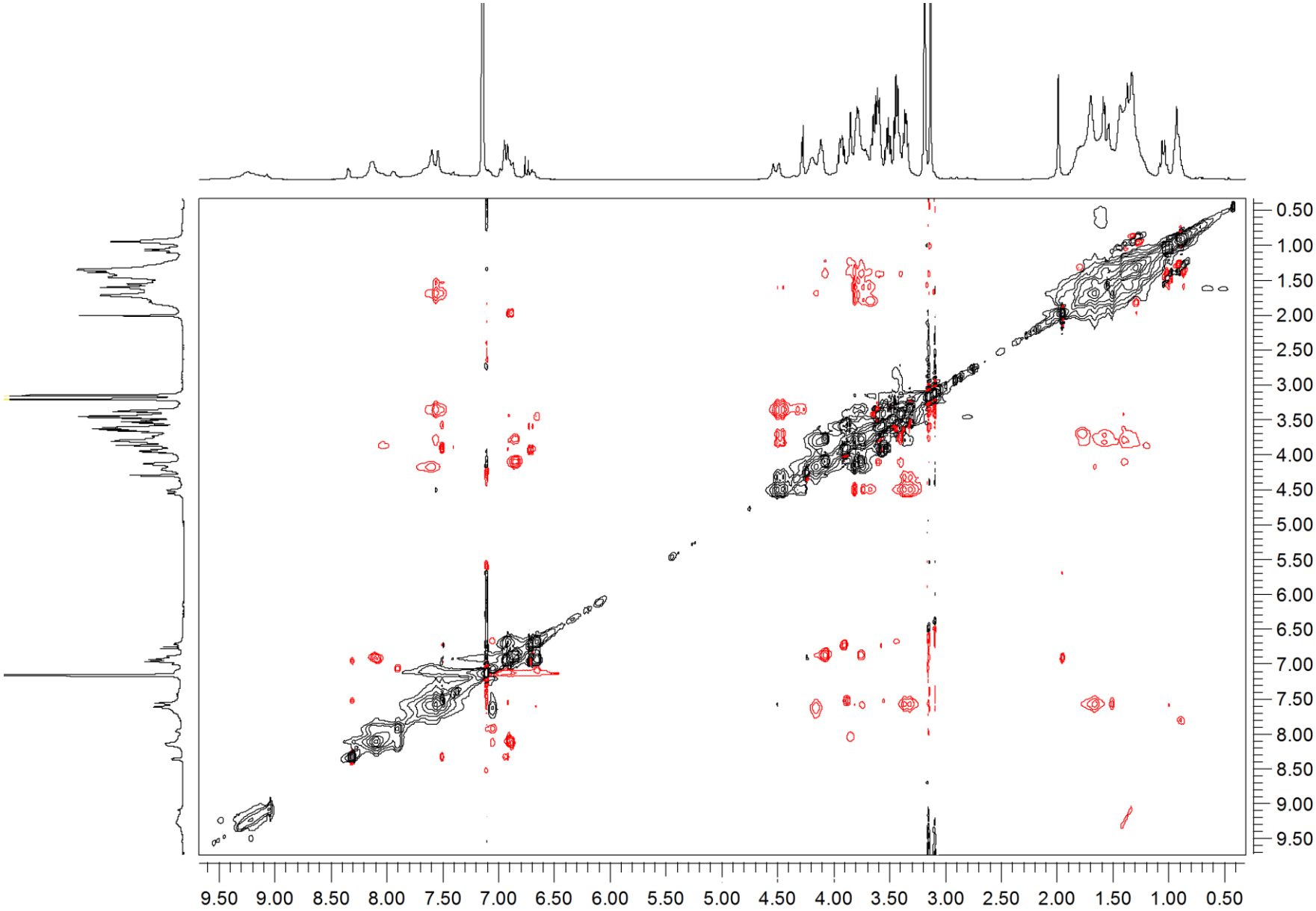


Figure S-5. 2D ROESY NMR spectra (300 MHz, C_6D_6, ROESY spin lock = 200 ms) of pseudorotaxane **P**[**CA8⊃DOV**]

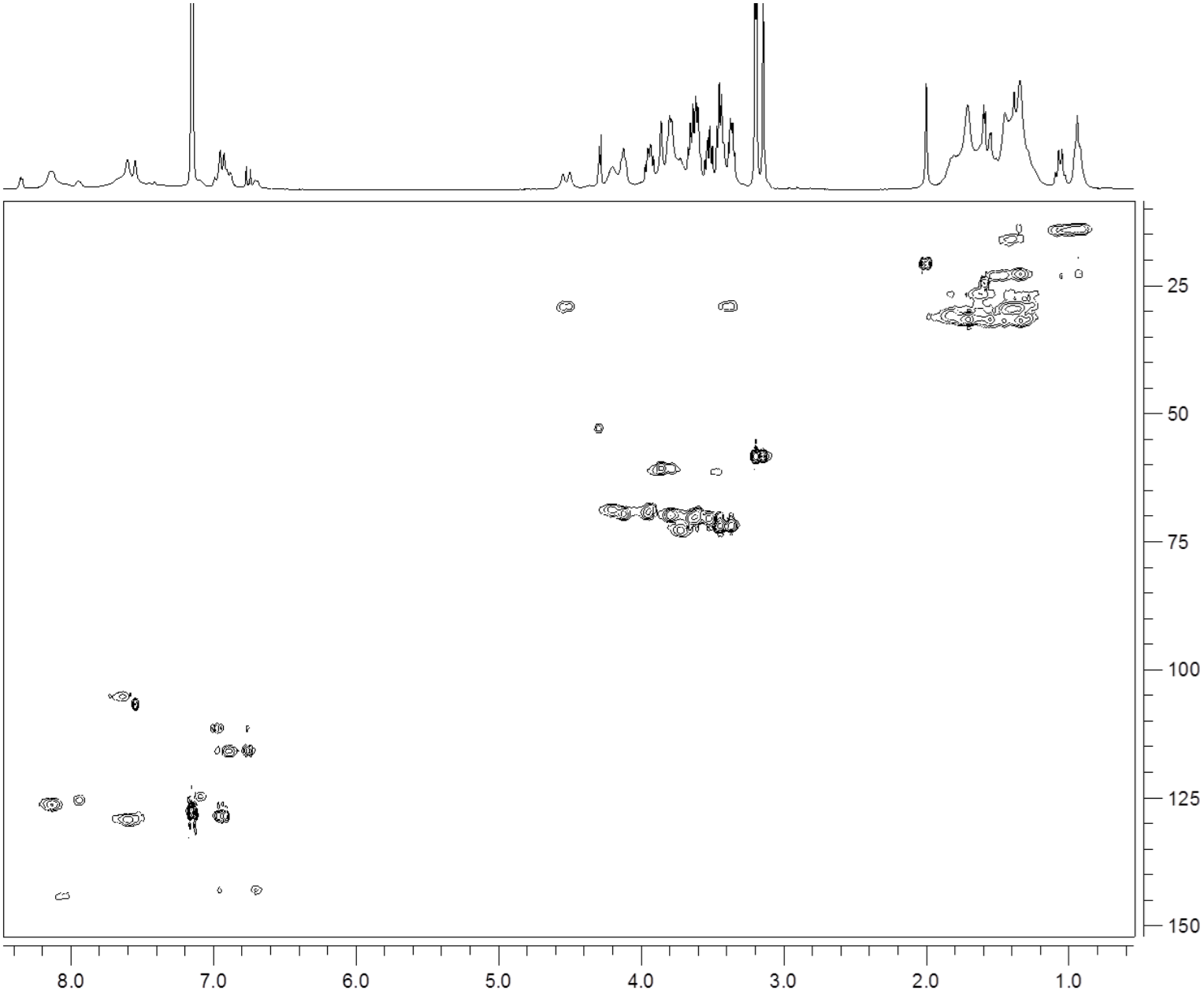


Figure S-6. 2D HSQC NMR spectra (300 MHz, C_6D_6) of pseudorotaxane **P[CA8⊃DOV]**

UV-Visible spectroscopic titration

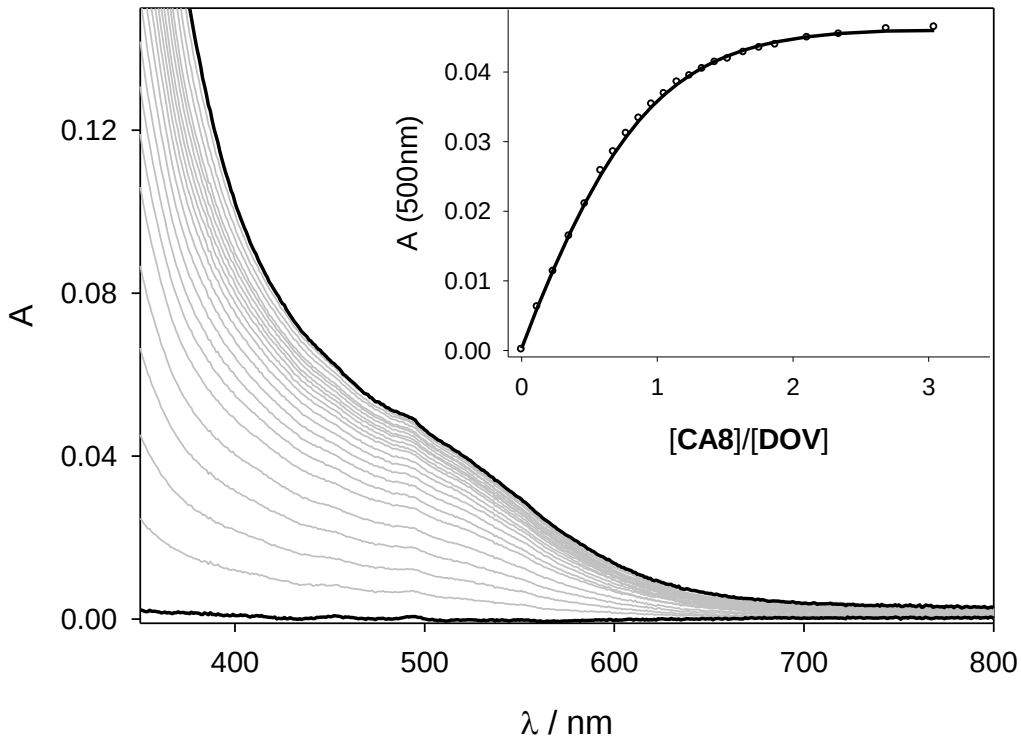
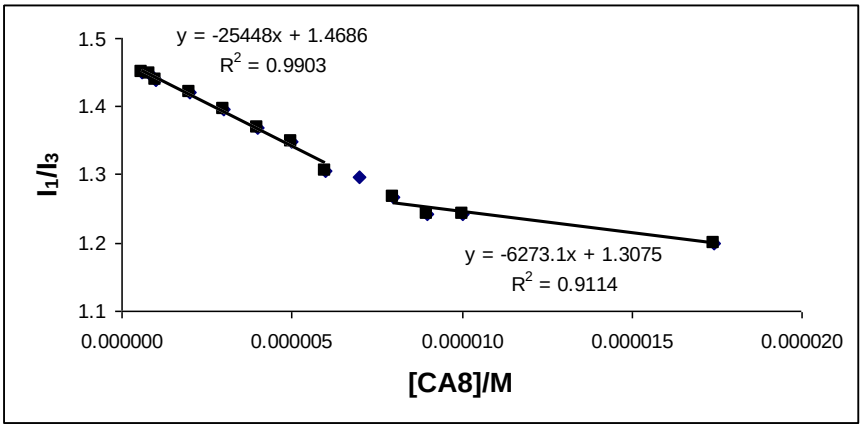


Figure S-7. Absorption spectra of a CH_3CN solution of **DOV** 1.24×10^{-4} M upon titration with **CA8** (room temperature; optical path length, 1 cm). The inset shows the absorption changes at 500 nm (empty circles) and the fitting of the experimental data according to a 1:1 binding model (solid line), corresponding to an association constant of 3.6×10^4 M^{-1}. The pseudorotaxane formation could not be investigated in water because the small spectroscopic changes related to the association process could not be detected at concentrations below c.a.c.

Determination of the critical aggregation concentration

A



B

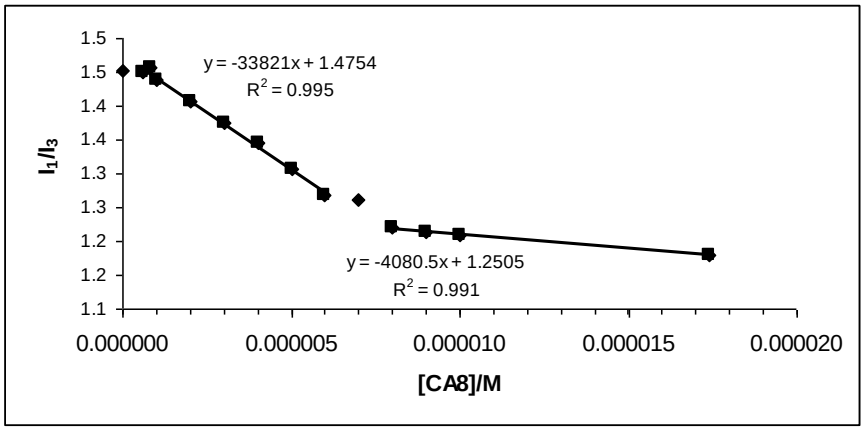
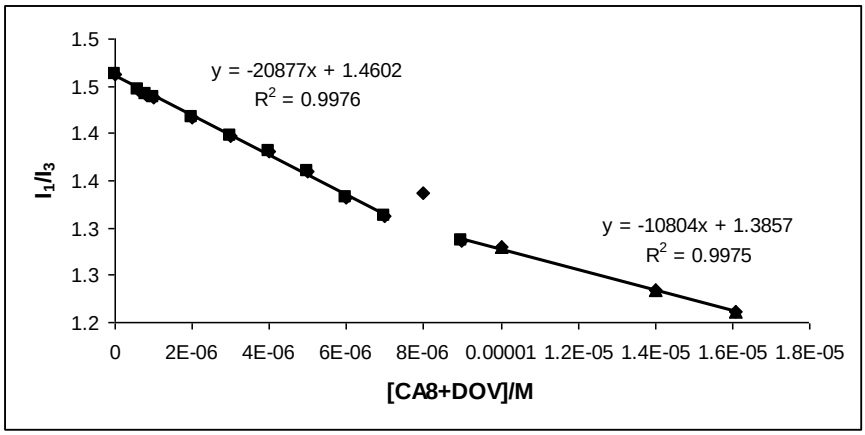


Figure S-8. C.a.c. determination of **CA8**. Two samples were performed: sample A and B.

A



B

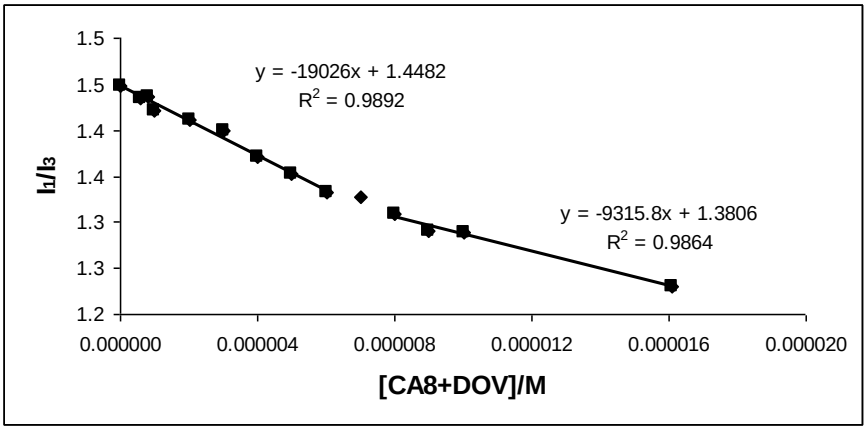
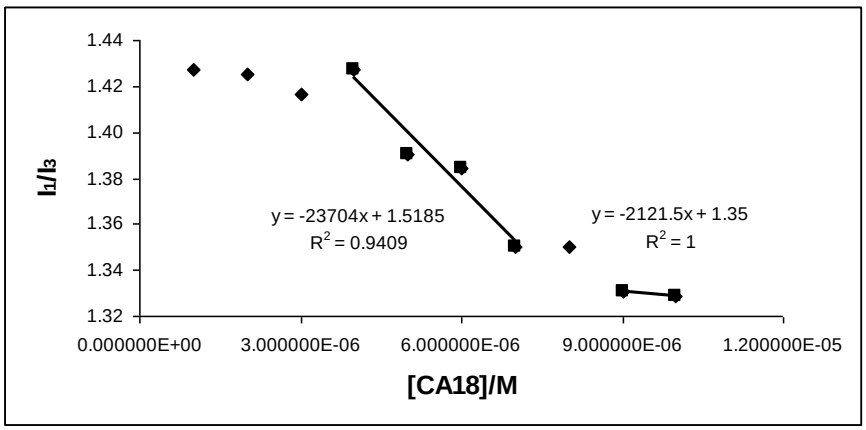


Figure S-9. C.a.c. determination of **CA8+DOV**. Two samples were performed: sample A and B.

A



B

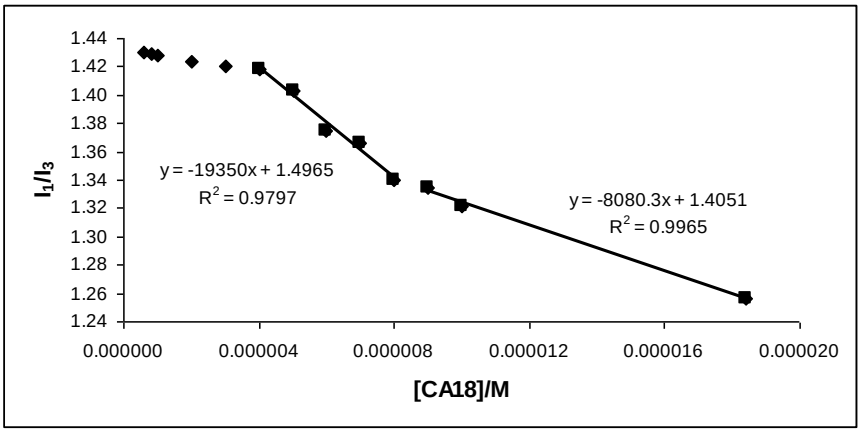


Figure S-10. C.a.c. determination of **CA18.** Two samples were performed: sample A and B.

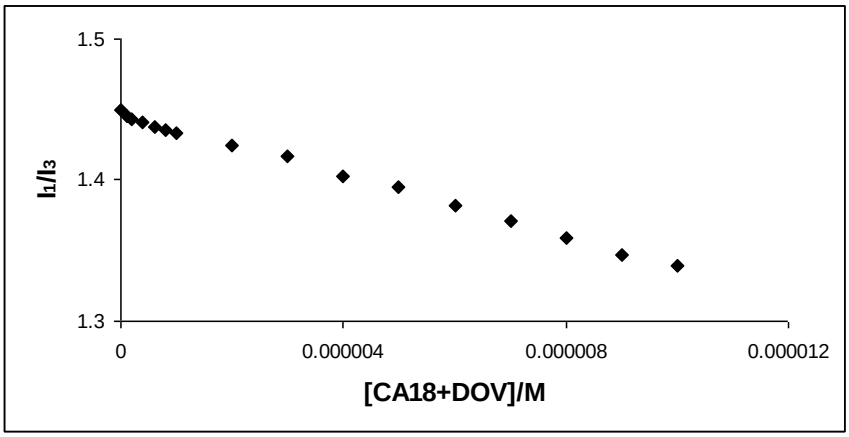


Figure S-11 C.a.c. determination of **CA18+DOV.**

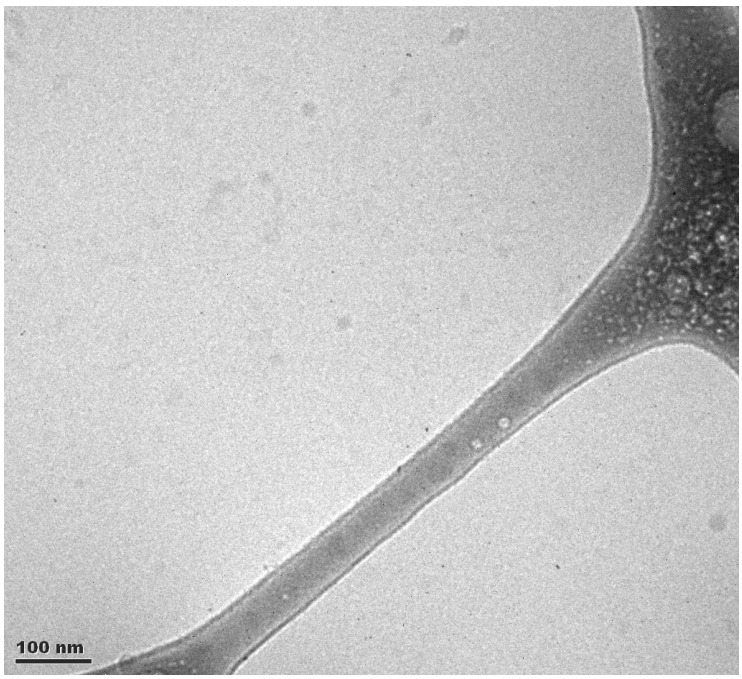


Figure S-12. Cryo-TEM of self-assembled **CA8**. Scale bar is 100 nm.

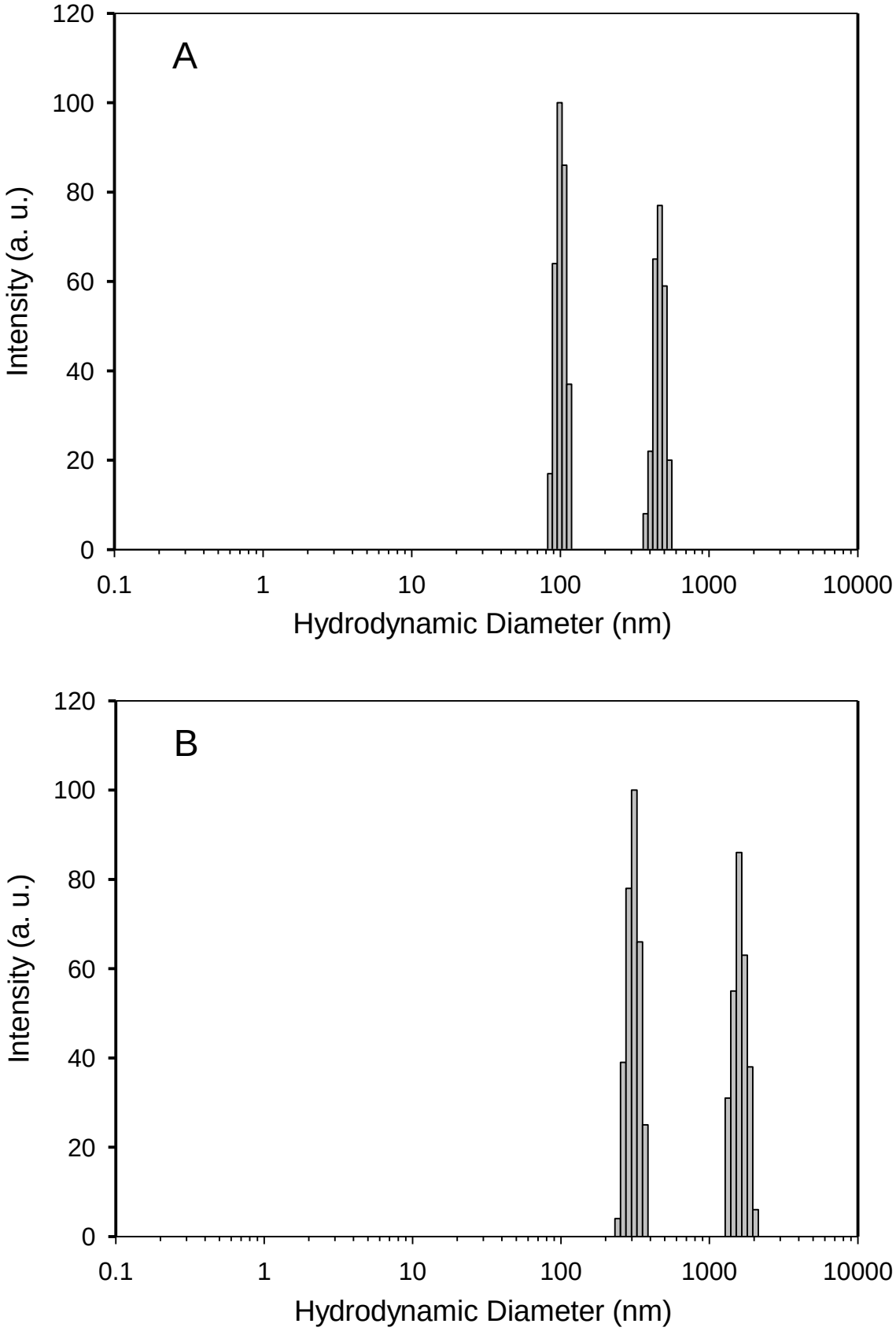


Figure S-13. DLS analysis of a 2×10^{-5} M aqueous sample of **CA8** in the absence (A) and in the presence (B) of **DOV**.

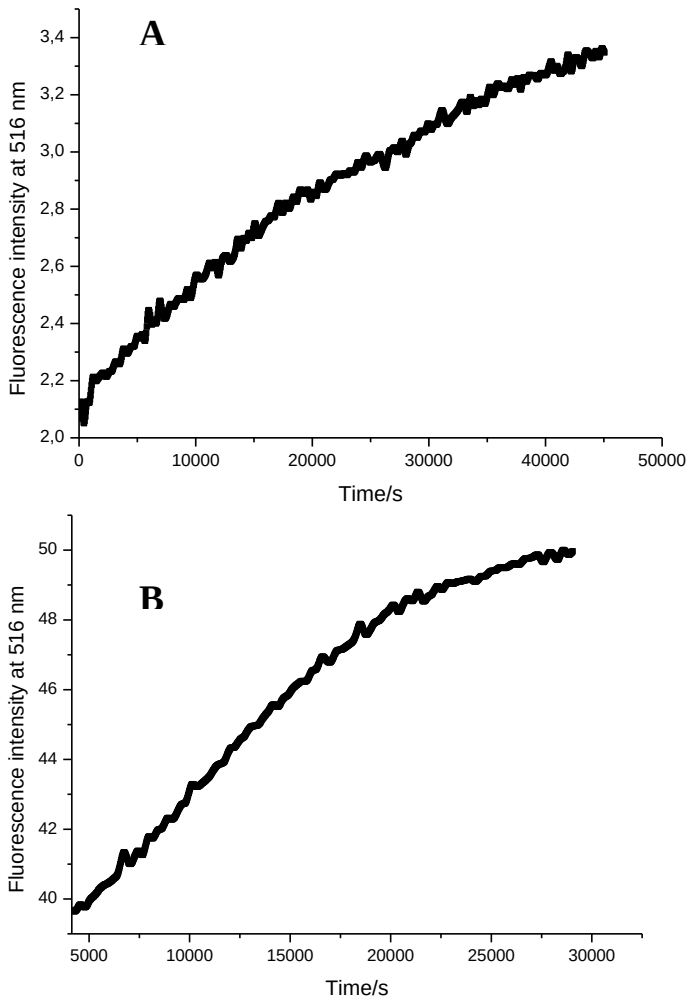


Figure S-14. Release of **CF** from A) **CA8** and B) **CA8+DOV** aggregates.

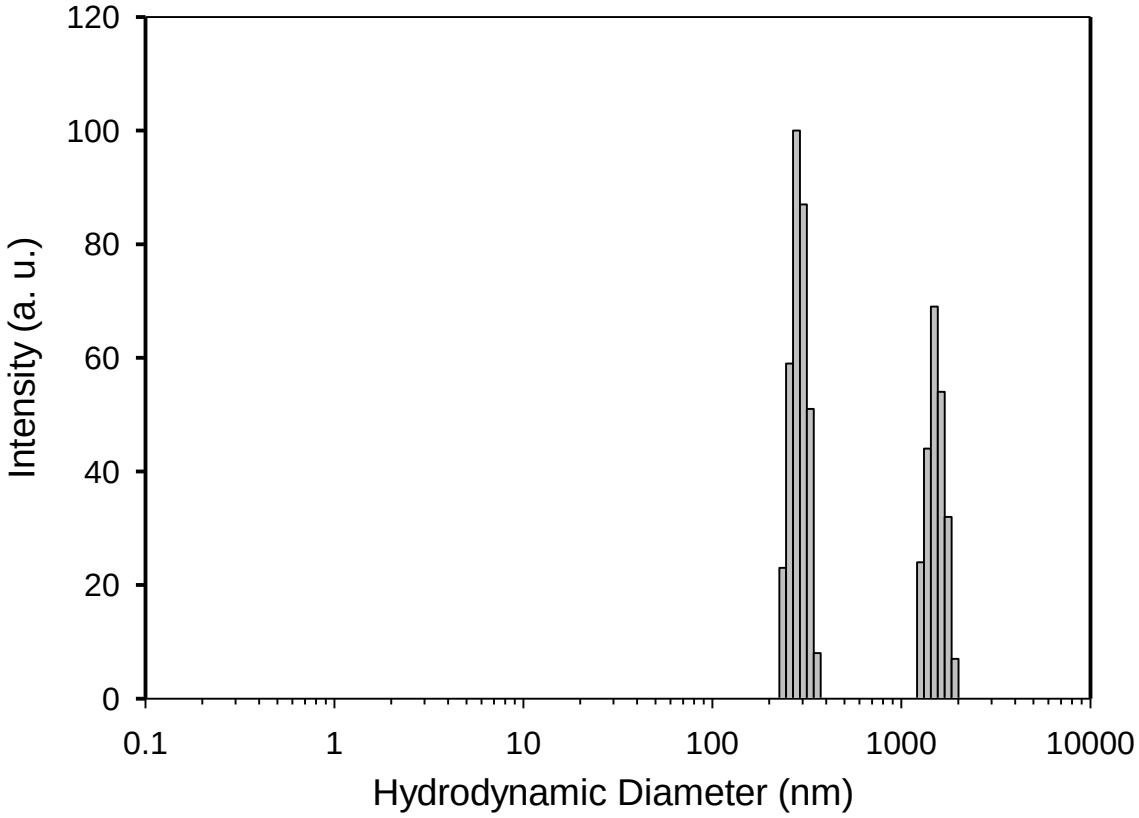


Figure S-15. DLS analysis of a 1.5×10^{-5} M aqueous sample of **CA18**.

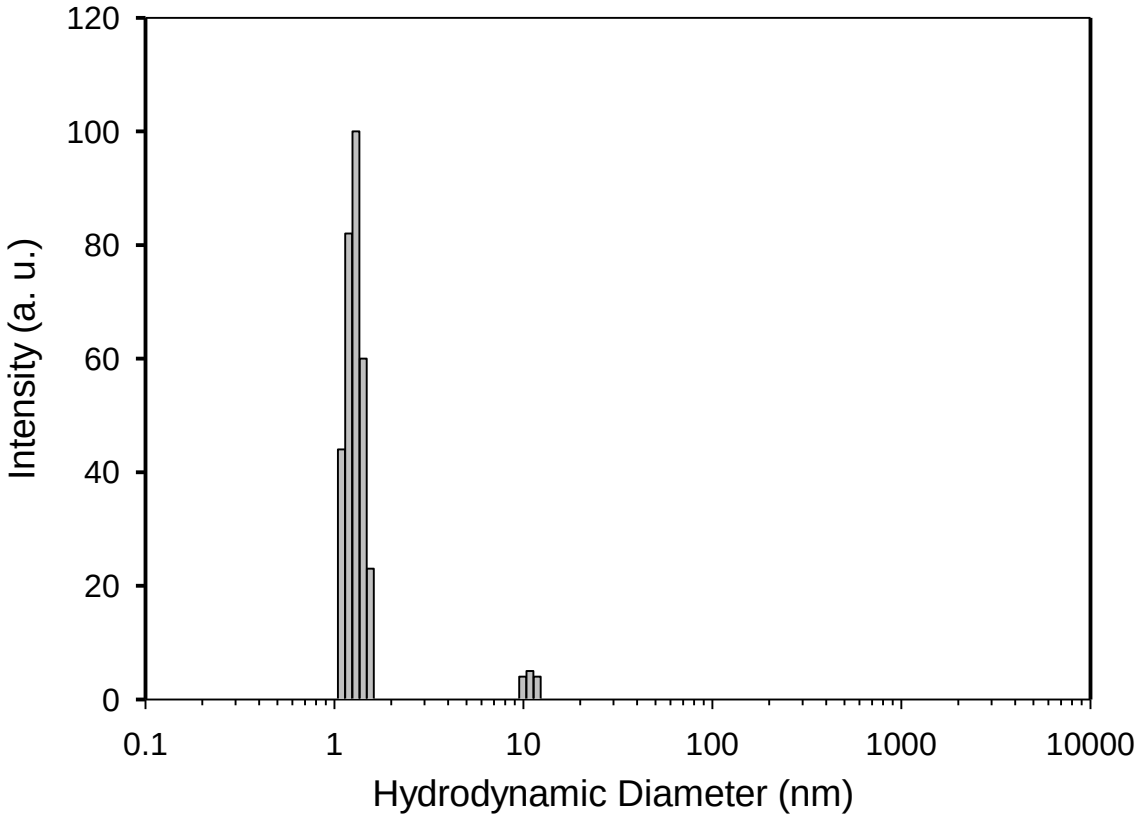


Figure S-16. DLS analysis of a 7.7×10^{-6} M aqueous sample of **C8**.