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ARTICLE TYPE

Electronic Supporting Information. Pseudorotaxane Formation Affected by Stereo-Electronic Effects. A Theoretical and Experimental Study

Rodolfo D. Porasso,[a] Matias I Sancho,[b] Mercedes Parajó,[c] Luis García-Río*[c] and Ricardo D. Enriz*[b]

1 ^{1}H NMR spectra characterization of compounds I-VIII

- **Bolaform I.** 1H-RMN (300 MHz, D_2O, ppm): δ = 8.86 (s, 4H), 8.57 (s, 2H), 8.08 (s, 4H), 4.62 (t, 4H), 2.02 (t, 4H), 1.34 (s, 4H) y 1.25 (s, 12H).
- **Bolaform II.** 1H-RMN (300 MHz, DMSO-d6, ppm): δ = 8.93 (d, 4H), 7.99 (d, 4H), 4.52 (t, 4H), 2.60 (t, 6H), 1.87 (t, 4H) y 1.23 (m, 16H).
- **Bolaform III.** 1H-RMN (300 MHz, DMSO-d6, ppm): δ = 9.07 (s, 2H), 8.97 (d, 2H), 8.45 (d, 2H), 8.06 (t, 2H), 4.56 (t, 4H), 1.91 (t, 4H) y 1.25 (m, 16H).
- **Bolaform IV.** 1H-RMN (300 MHz, DMSO-d6, ppm): δ = 8.99 (d, 2H), 8.47 (t, 2H), 8.04 (d, 2H), 7.97 (t, 2H), 4.52 (t, 4H), 2.84 (s, 6H), 1.83 (t, 4H), 1.32 (s, 4H) y 1.26 (s, 12H).
- **Bolaform V.** 1H-RMN (300 MHz, D_2O, ppm): δ = 8.50 (s, 2H), 8.16 (d, 2H), 7.73 (d, 2H), 4.46 (t, 4H), 2.75 (s, 6H), 2.45 (s, 6H), 1.90 (t, 4H) y 1.30 (m, 16H).
- **Bolaform VI.** 1H-RMN (300 MHz, D_2O, ppm): δ = 8.12 (t, 2H), 7.64 (d, 4H), 4.44 (t, 4H), 2.83 (s, 12H), 1.85 (t, 4H) y 1.43 (m, 16H).
- **Bolaform VII.** 1H-RMN (300 MHz, D_2O, ppm): δ = 8.47 (s, 4H), 8.18 (s, 2H), 4.48 (t, 4H), 2.49 (s, 12H), 1.96 (t, 4H) y 1.26 (d, 16H).
- **Bolaform VIII.** 1H-RMN (400 MHz, D_2O, ppm): δ = 3.30 (t, 4H), 3.11 (s, 1H), 1.79 (s (width), 4H), 1.37 (s, 4H) y 1.30 (s, 12H).

[a] *Instituto de Matemática Aplicada San Luis (IMASL), CONICET. Facultad de Ciencias Físico Matemáticas y Naturales, Universidad Nacional de San Luis, Av. Ejército de los Andes 950, 5700, Argentina.*
[b] *Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis; Instituto Multidisciplinario de Investigaciones Biológicas (IMIBIO-SL). Chacabuco 915, 5700 San Luis, Argentina.*
[c] *Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago, Spain.*
∗ Corresponding authors: deriz@unsl.edu.ar and luis.garcia@usc.es

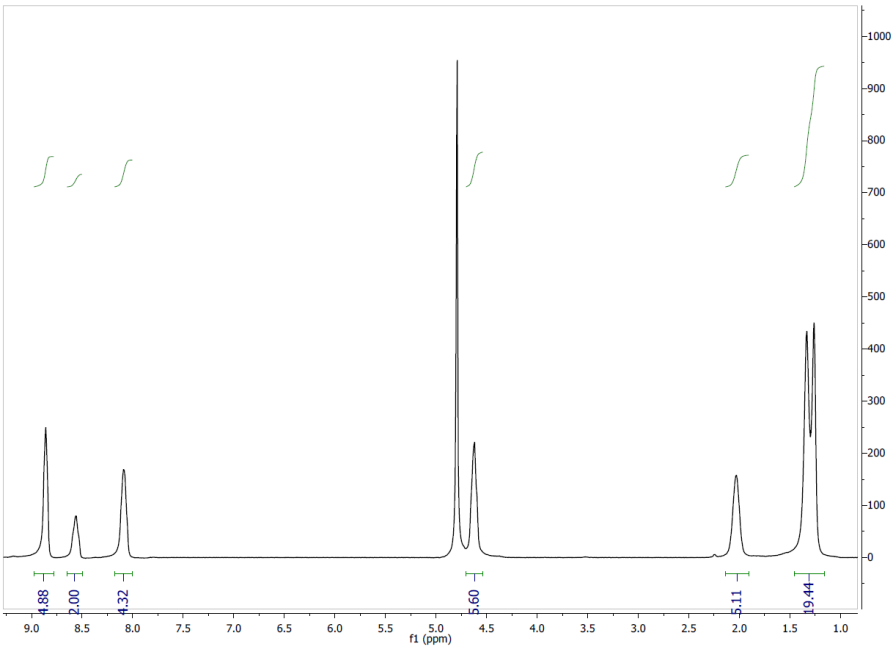

Fig. ESI 1 1H NMR spectrum of **bolaform I** in D_2O.

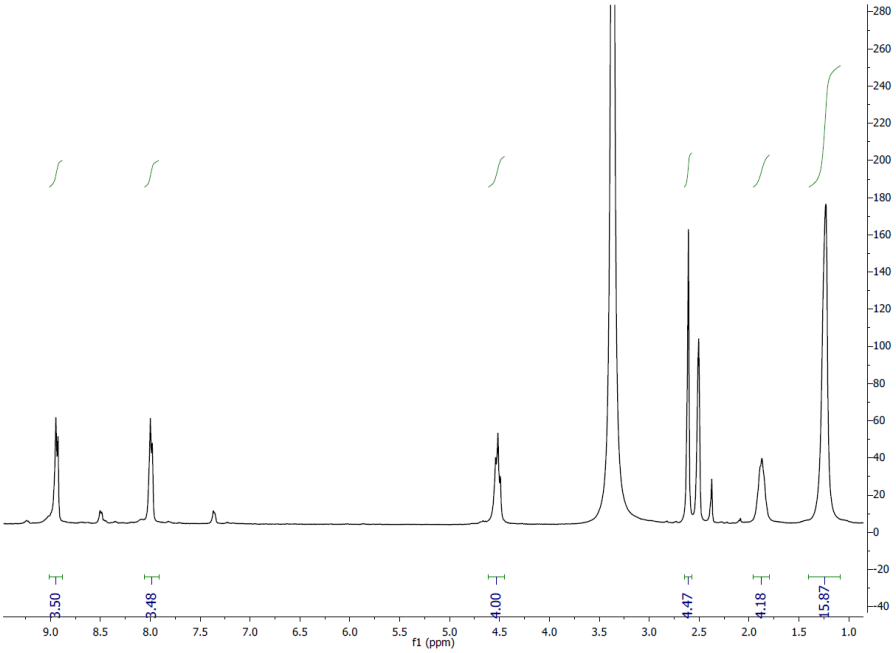

Fig. ESI 2 1H NMR spectrum of **bolaform II** in DMSO-d9.

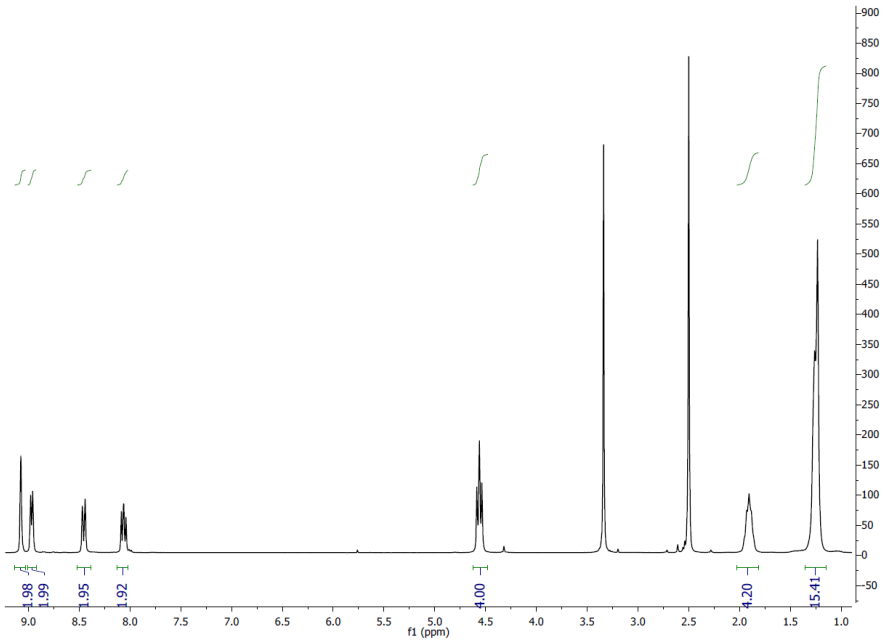

Fig. ESI 3 1H NMR spectrum of **bolaform III** in DMSO-d9.

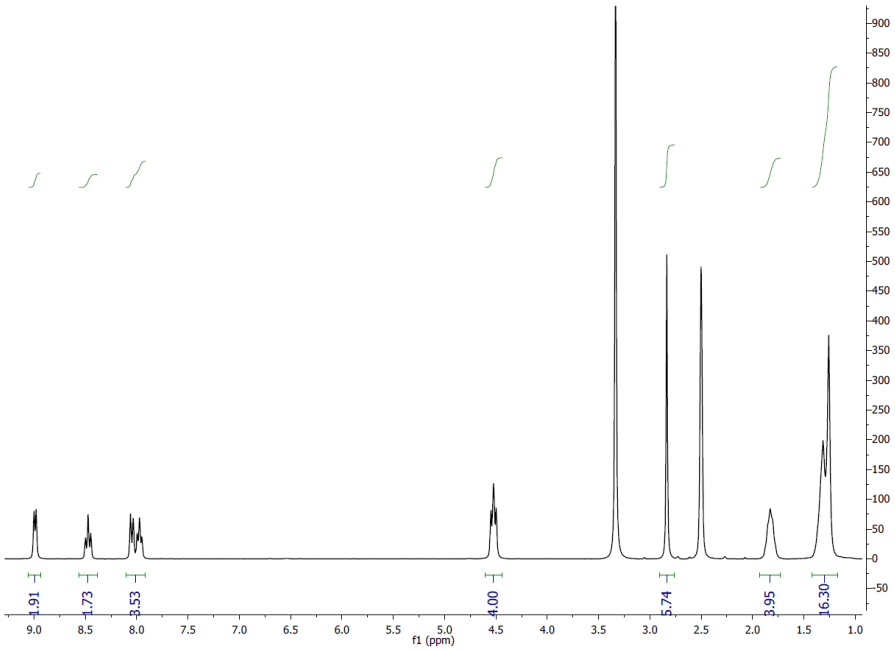

Fig. ESI 4 1H NMR spectrum of **bolaform IV** in DMSO-d9.

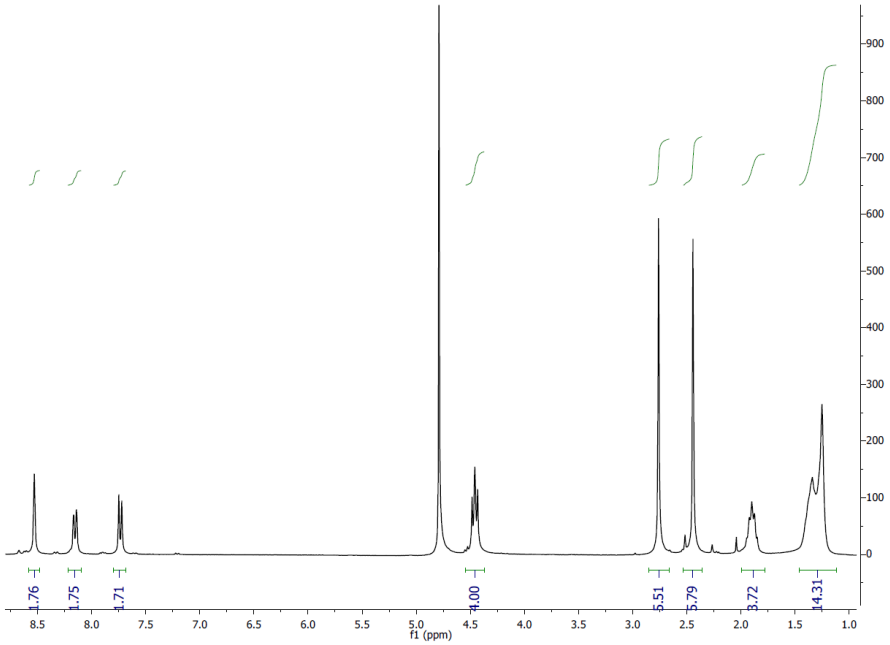

Fig. ESI 5 11H NMR spectrum of **bolaform V** in D_2O.

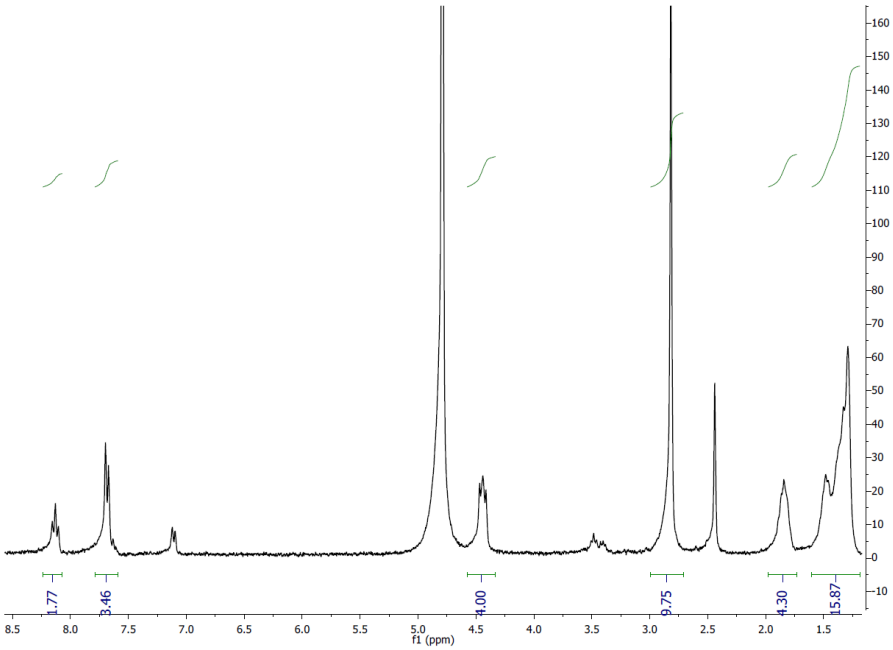

Fig. ESI 6 1H NMR spectrum of **bolaform VI** in D_2O.

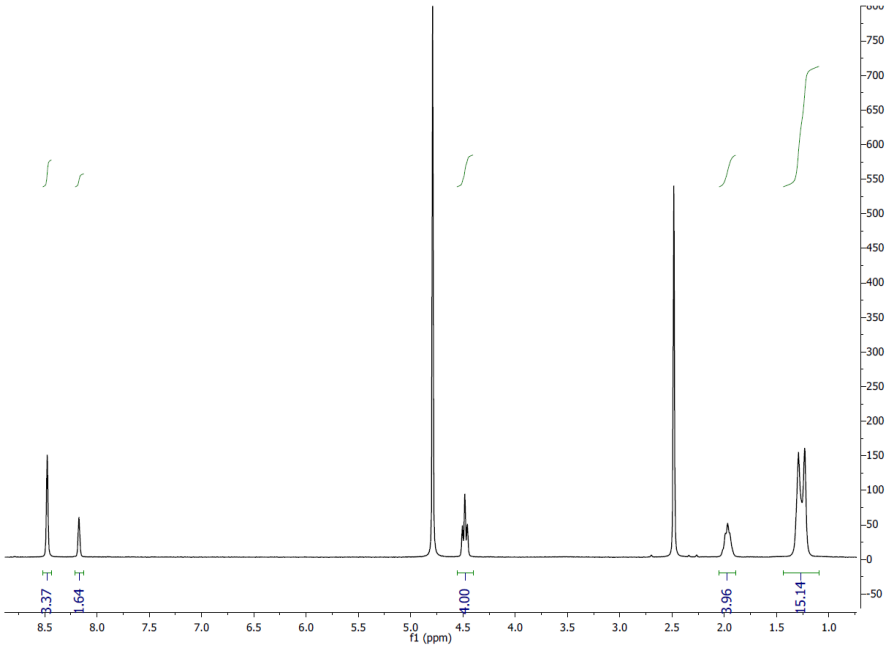

Fig. ESI 7 1H NMR spectrum of **bolaform VII** in D_2O.

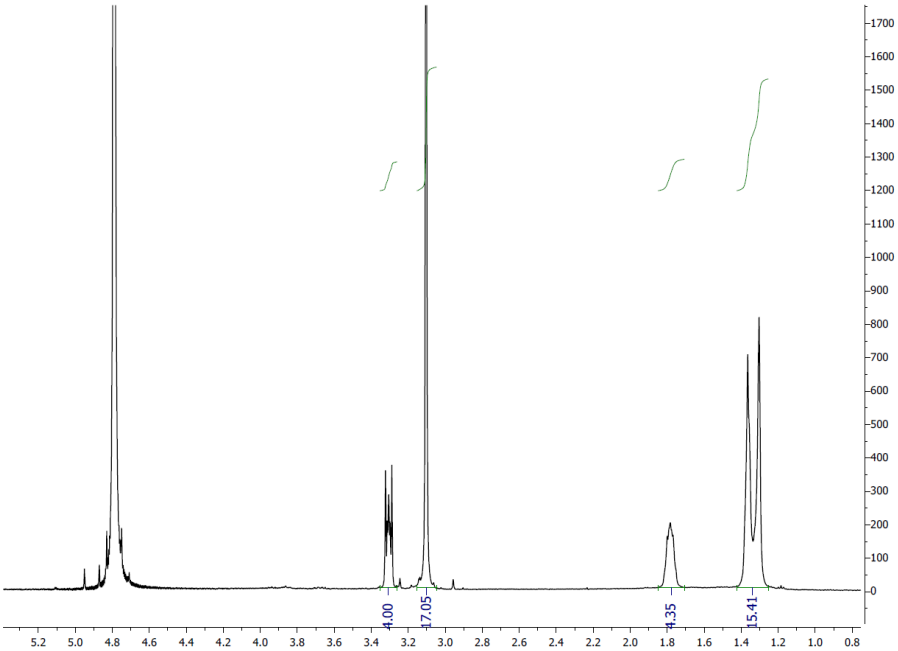

Fig. ESI 8 1H NMR spectrum of **bolaform VIII** in D_2O.

2 MEPS

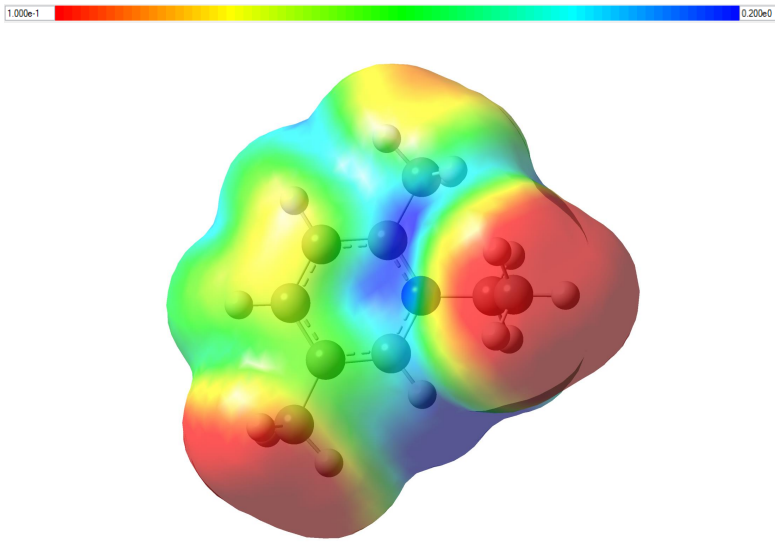

Fig. ESI 9 Electrostatic potential-encoded electron density surfaces obtained for the pyridinium rings of Axle V.

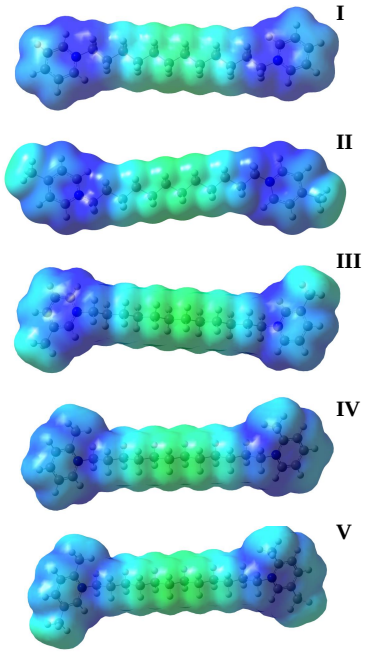

Fig. ESI 10 Electrostatic potential-encoded electron density surfaces obtained for Axles I-V.

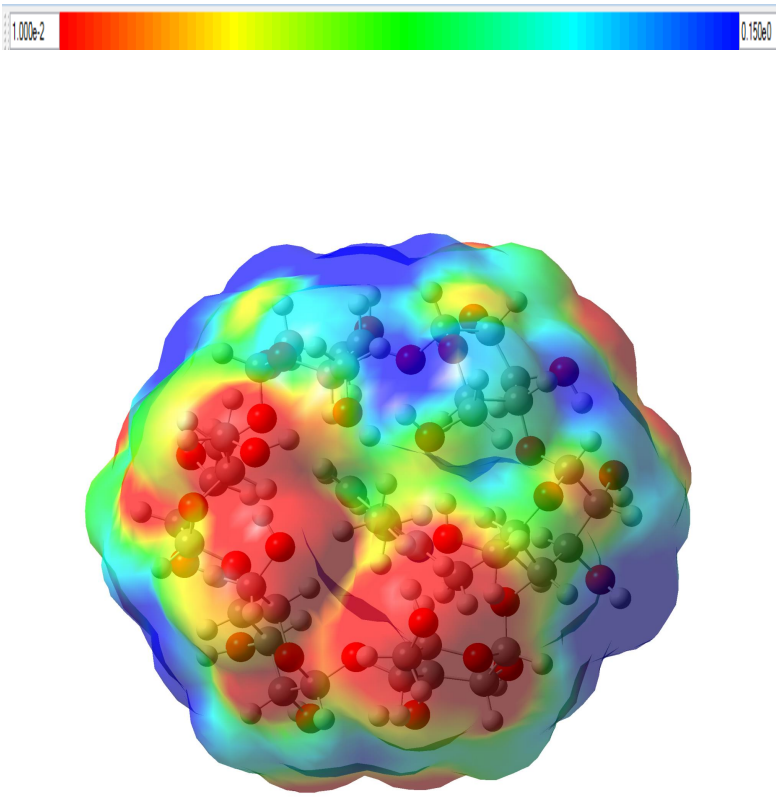

Fig. ESI 11 Map of electrostatic potential for the Axle α–CD:V system.

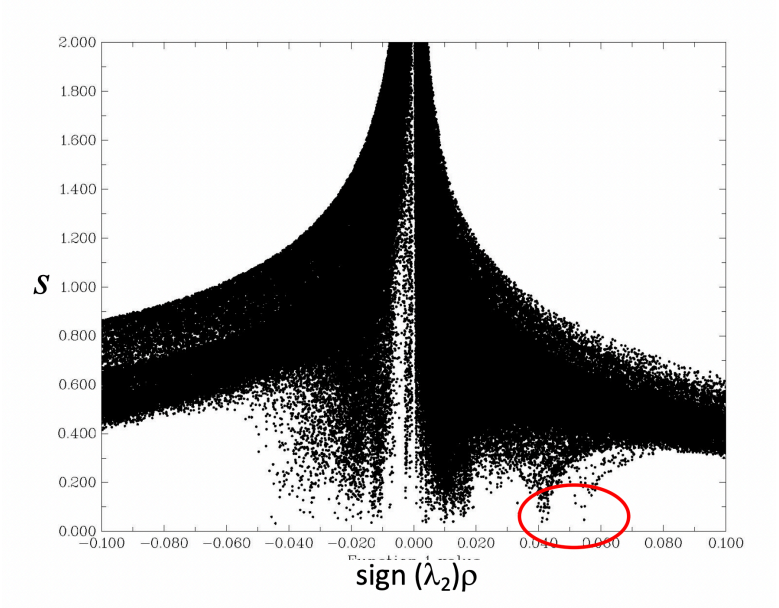

Fig. ESI 12 Scatter plot of S (RDG) vs sign $(\lambda_2)\rho$ calculated for the Axle V:α–CD system.

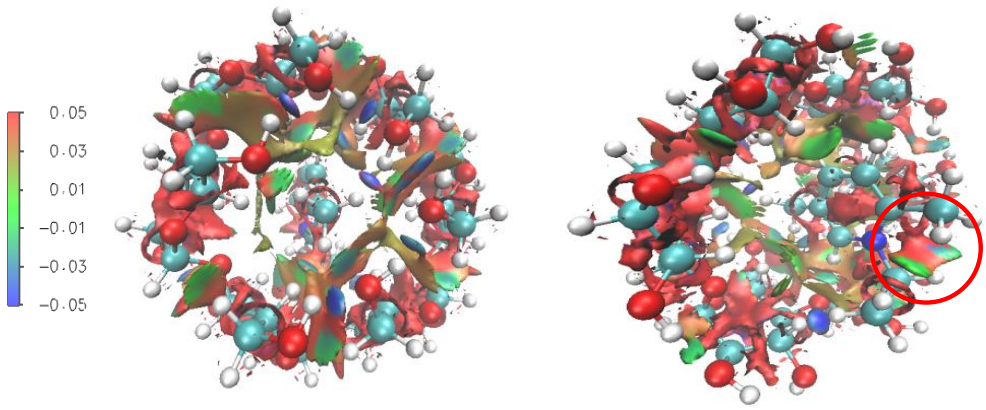

Fig. ESI 13 Front (left) and back (right) RDG base isosurfaces ($s = 0.5$a.u.) of Axle V:α−CD complex colored on a scale according to sign $(\lambda_2)\rho$ values.

3 Free energy calculations

In Figure 14 the window overlapping obtained from the Umbrella Sampling MD simulations in depicted for the α–CD:Axle I system, when the Axle is inserted from the Head side of the cyclodextrine. As can be appreciated a good overlapping between the different windows simulations is obtained.Note that a denser overlap is obtained in the region -1.6 nm $< \xi < 0$ nm as is detailed in Section 2.4.2. For the other 16 Umbrella Sampling MD simulations, corresponding to the 8 systems when the bolaform is inserted for the both sides of the α–CD, similar results are obtained and they are omitted for the sake of brevity.

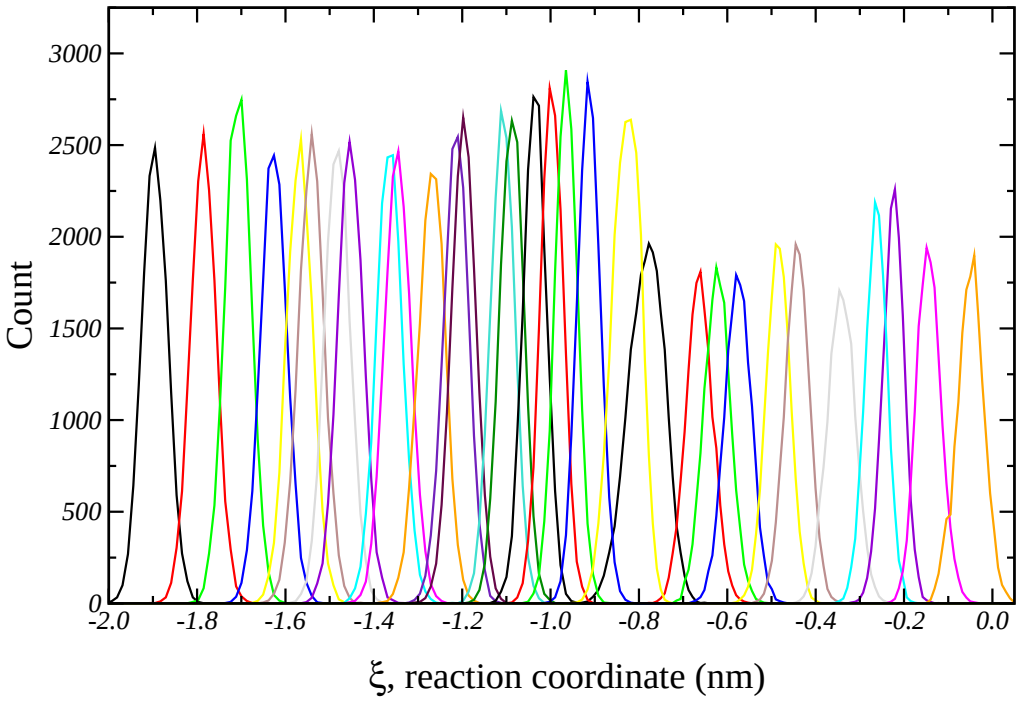

Fig. ESI 14 Windows overlapping for the α–CD:Axle I system, obtained from Umbrella Sampling MD simulations.