

Electronic Supplementary Information for

**Highly Charged Supramolecular Oligomers Based on the
Dimerization of Corannulene Tetraanion**

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Experimental methods

Bicorannulenyl was prepared as described earlier.¹ Reduction was carried out at dry ice temperature in narrow NMR tubes ($\phi = 4$ mm), under argon atmosphere (approximate pressure 0.7 atm), with THF- d_8 as the solvent. The tube was fitted with an extension, which contained a fresh lithium wire. The yellow solution turned deep purple after several hours of contact with the lithium metal,² and finally turned dark brown after approximately 24 hours of contact.

The SD-NMR experiments were performed in narrow tubes to minimize eddy currents, with the solvent serving as an internal reference. Measurements were repeated at least three times. The pulse sequence employed was bipolar longitudinal eddy-current delay (BPLED) and it was tested that stimulated echo and bipolar standard stimulated echo give similar results, in view of the concern raised by Avram and Cohen.³ To derive diffusion constants from the SD-NMR experiments we fitted an exponential function to the signal decay, rather than employed the diffusion ordered spectroscopy (DOSY) technique. While the latter provides a convenient 2D map of chemical shift versus diffusion constant (Fig. 3 in the Communication), the diffusion constants it produces are less accurate (especially in cases of low spectral resolution), and the DOSY technique in general is more prone to artifacts and less sensitive to identification of bi-exponential decays.

Analysis of SD-NMR experiments

To determine the degree of polymerization (n) of the aggregates, their sizes are first estimated from the diffusion constants, and then n is derived using a reasonable model for polymer folding.

According to the corrected Stokes-Einstein equation, the hydrodynamic radius (R_H) depends inversely on the diffusion constant (D):

$$D = \frac{kT}{c(R_{\text{soln}}, R_H) f_S \pi \eta R_H}$$

where k is the Boltzmann constant, T is the absolute temperature, η is the fluid viscosity, $c(R_{\text{solv}}, R_{\text{H}})$ is the size factor that depends on the size of the solute and solvent molecules, and f_{s} is the shape factor.⁴ For small- or medium-sized molecules with somewhat non-spherical shapes, the size and shape corrections are small and tend to cancel out, partially or completely.⁴ As a result, we may assume for the bicorannulenyl octaanion oligomers that $D^{\text{polymer}} / D^{\text{neutral}}$ is a very good estimate for $R_{\text{H}}^{\text{neutral}} / R_{\text{H}}^{\text{polymer}}$.

As to the polymer folding model, the flexible oligomers⁵ would be best described as Gaussian (real) chains with excluded monomer volumes.⁶ For such polymers $R_{\text{H}} \propto n^{\nu}$, where $\nu = 0.6$ (the Flory exponent) in a good solvent. Thus the following equation for the number of repeating units is obtained:

$$n = \left(\frac{D^{\text{polymer}}}{D^{\text{neutral}}} \right)^{\frac{1}{\nu}}$$

References

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- (2) D. Eisenberg, E. A. Jackson, J. M. Quimby, L. T. Scott and R. Shenhar, *Angew. Chem. Int. Ed.*, 2010, DOI: 10.1002/anie.201002515.
- (3) L. Avram and Y. Cohen, *J. Am. Chem. Soc.*, 2005, **127**, 5714-5719.
- (4) For a comprehensive review, see A. Macchioni, G. Ciancaleoni, C. Zuccaccia and D. Zuccaccia, *Chem. Soc. Rev.*, 2008, **37**, 479-489.
- (5) The chains consist of flexible joints: the central bond of **2** and the weak bond between two corannulene moieties.
- (6) I. Teraoka, *Polymer Solutions: An Introduction to Physical Properties*, New York, John Wiley & Sons, Inc., 2002.