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Supplementary information for: Self-assembly of web of nanorings revised: evidence of solvent-mediated growth of semiflexible coordination polymer

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SI1 Estimation of hypothetical vesicle size

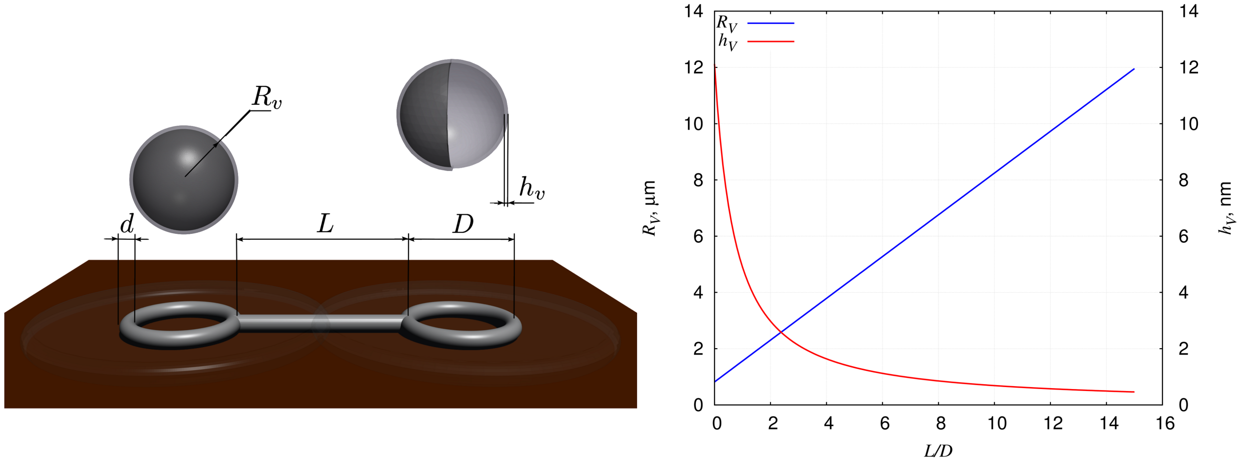

Figure S1 Schematic representation of a vesicle piercing mechanism (left) and radius and thickness of the hypothetical vesicle required to form the ring of diameter D, connected with rods of length L as a function of L/D (right)

Taking for consideration a critical case, in which the contacts form only as the vesicle is completely deflated and maximally spread over the substrate surface (figure S1) it is straightforward to estimate the radius of initial vesicle (R_v) and its thickness (h_v) from the surface area of deflated vesicle (S_v) and volume of the final ring (V_R) of diameter D including also half the volume of the 3 rods of length L and thickness d, equal to the thickness of the ring's rim:

$$\begin{gathered} S_v = 2 \times \pi((D+L)/2)^2 + 0.5 \times \pi d \times \pi(D+L); \\ V_R = \pi D \times \pi(d/2)^2 + 3 \times \pi(d/2)^2(L/2); \\ R_v = \sqrt{\frac{S_v}{4\pi}}; \quad h_v = \frac{V_R}{S_v}. \end{gathered} \tag{S1}$$

Evolution of vesicle radius and thickness with increase of desired rod length is demonstrated by the figure S1. Rapid decrease of thickness down to the size of a single compound molecule makes the explanation of the rod formation via vesicle piercing, proposed in Ref. 1, quite questionable for the rods with length up to $\sim 15\,\mu$m.

SI2 Comparison of bis-salphen compounds studied in the referred paper

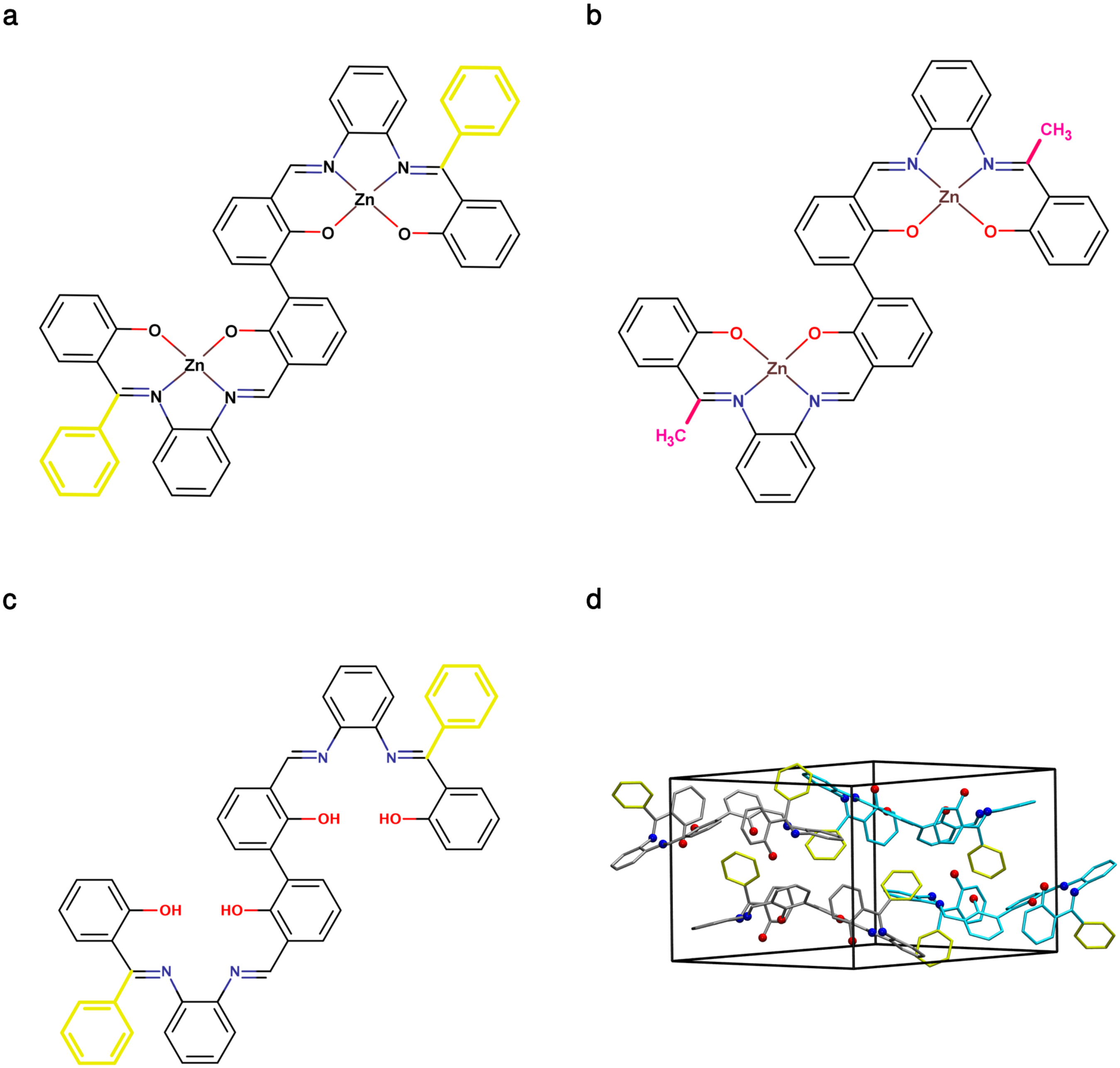

Figure S2 Chemical structures of phenyl- (a) and methyl-functionalized (b) bis-Zn(salphen) compounds, as well as of unsubstituted bis-salphen ligand (c) and its unit cell (d), resolved from X-ray studies[1], backbone color is used to highlight the two pairs of molecules with opposite orientation; image produced using Tachyon ray tracer as implemented in VMD software[2,3]; hydrogens are omitted for clarity, functional phenyl and methyl side-groups are shown with yellow and pink correspondingly; MarvinSketch was used for drawing, displaying and characterising chemical structures, substructures and reactions[4]

SI3 Interaction of isolated bis-Zn(salphen) complexes with explicit solvent

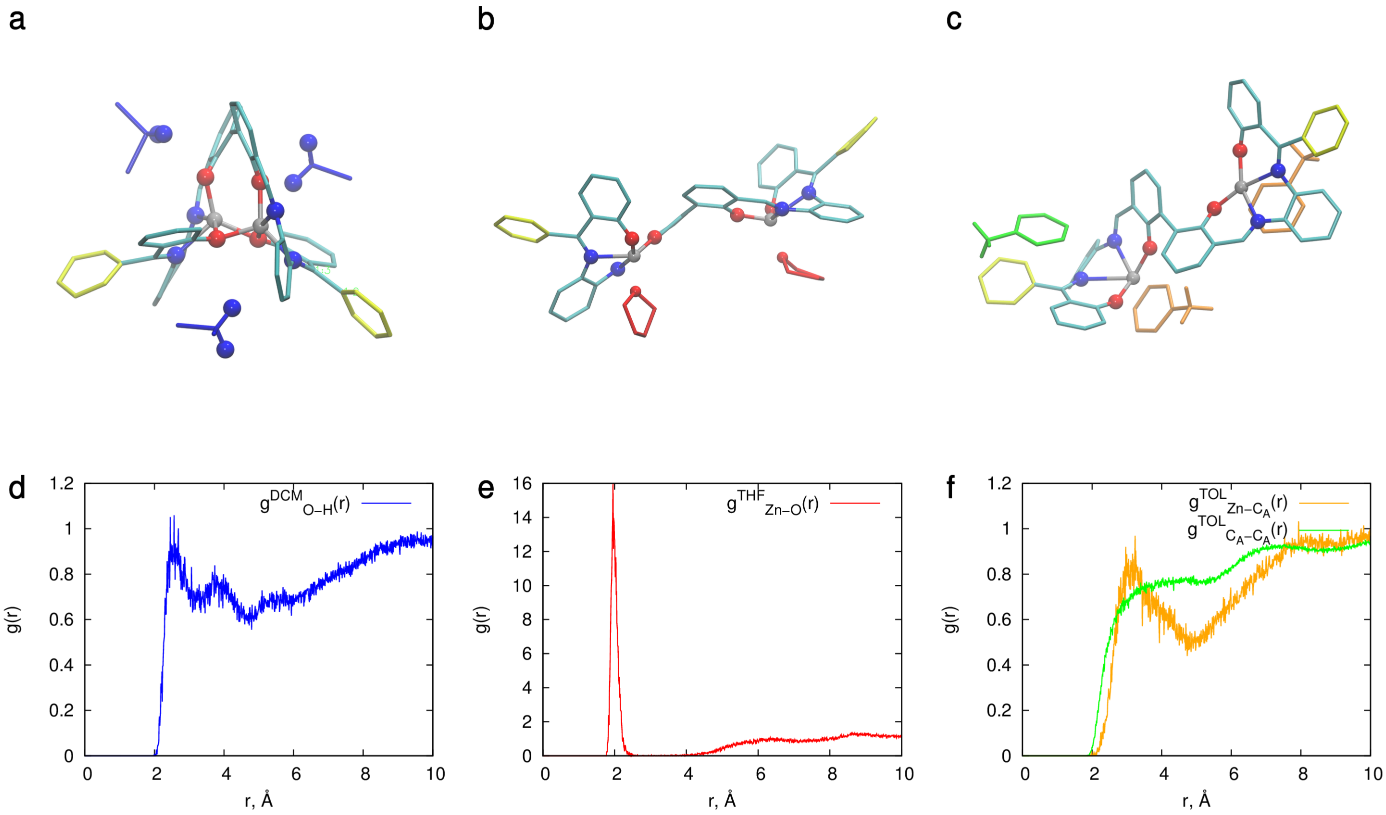

Figure S3 Interaction of a single bis-Zn(salphen) complex with DCM (a), THF-oxygen (b) and toluene (c) and radial distribution functions for the corresponding atom types (d,e,f); DCM-hydrogen and THF-oxygen atoms are indicated with spheres on the solvent molecule

SI4 Validation of compound molecule parametrization with DFT calculations

One problem that requires special attention is the applicability of the force field based modelling to the system of interest. This is especially important for metal-organic complexes like the one studied here as the charge distribution of such complexes might fluctuate depending on the geometry of the complex and its environment, impacting the dynamics of the molecule. To verify that the chosen parametrization stays valid we have compared the geometries of several reference compounds and their dimers (figure S4) optimised with LAMMPS against the result of density functional theory (DFT) electronic structure calculations in ONETEP.

The initial coordinates of single bis-Zn(salphen) complexes and their dimers in vacuum were derived from X-ray resolved reference geometries in Ref. 1. The root mean square deviation of atomic positions between GAFF and DFT optimised structures were found to be ≤ 0.15 in all cases. Binding energy difference of the order of a few $\mathrm{kcal/mol}$ ($< 10\%$) was estimated between DFT and GAFF approaches (Table S1). The Zn cation charge of $1.55 \pm 0.09 \left|e^-\right|$ was estimated according to natural bond orbital analysis (NBO) as implemented in ONETEP[5] across all systems used in this comparison.

Also, interaction potential profiles were estimated with the two approaches for the Zn-O bonded dimer of the mono-salphen complex (figure S5a). For this purpose one of the monomers was displaced in the 1 wide interval around optimal separation distance (r_0) fixing carbon-hydrogen backbone, but leaving oxygen and zinc atoms free to relax their positions. It can be seen from the resulting profiles that the chosen parametrization starts to deviate from DFT results only when the two monomers are pushed too close to each other, which seldom occurs in the simulation as shown by the distribution of Zn-O ionic bond lengths, calculated over all trajectories simulated in the current work. A similar comparison was also performed for the interaction between a single mono-salphen complex and a THF molecule (figure S5b), as this was one of the solvents used experimentally, for which strong ionic interaction could be expected.

These small deviations indicate that the chosen molecular model parametrization allows us to investigate the behaviour of zinc-salphen complexes in all cases of interest with a precision sufficient for the purpose of this study and at acceptable computational cost.

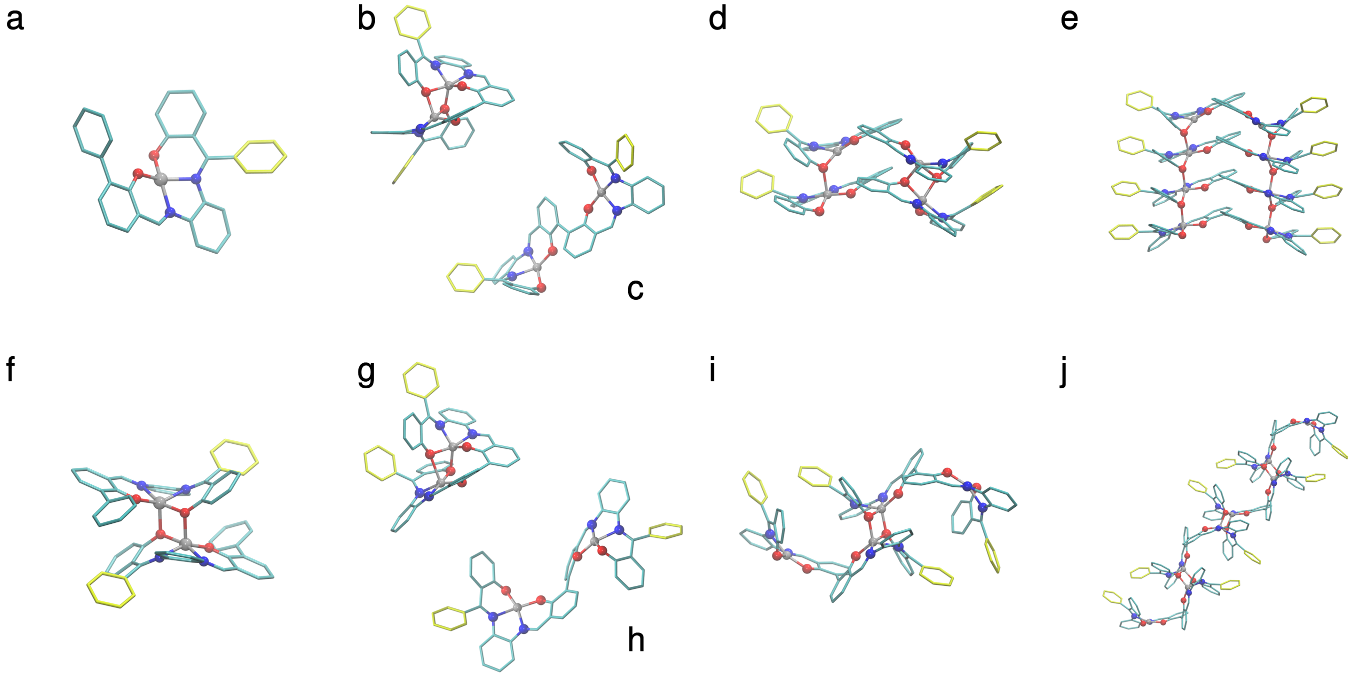

Figure S4 3D representation of the molecular structures optimised with ONETEP: (a) - a mononuclear Zn(salphen) compound from the reference work and its dimer (f), (b-c) and (g-h) - *W*- and *S*-shaped conformation of the compound under study in *closed* and *open* states correspondingly, (d-e) and (i-j) - dimer and tetramer structures corresponding to alpha (*W*-shaped) and beta (*S*-shaped) polymeric chains

Table S1 Binding energies of the selected structures, caluclated with DFT (ONETEP) and GAFF (LAMMPS)

	$\Delta E_{binding}$ (kcal/mol)		
Transition	DFT	GAFF	absolute error
$a \rightarrow f$	-49.5	-47.3	2.2
$b \rightarrow c$	-24.4	-23.7	0.7
$c \rightarrow d$	-62.4	-59.0	3.4
$d \rightarrow e$	-56.1	-54.3	1.8
$g \rightarrow h$	-20.6	-20.7	0.1
$h \rightarrow i$	-44.6	-48.5	3.9
$i \rightarrow j$	-39.7	-39.6	0.1

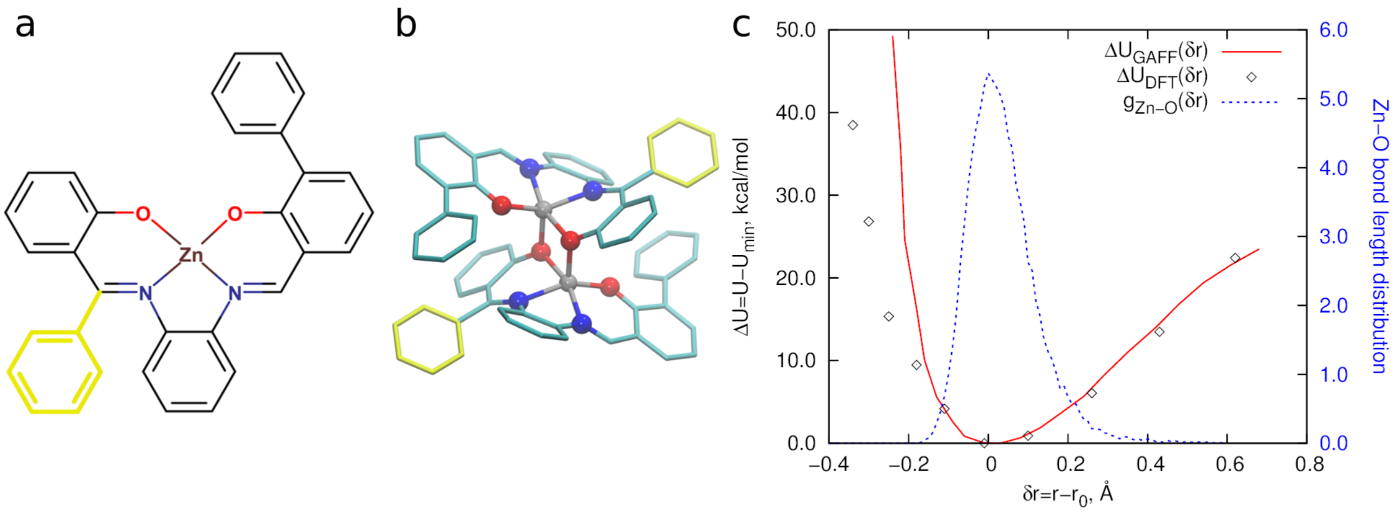

Figure S5 Schematic representation of mono-Zn(salphen) compound (a) and 3D structure of its Zn-O bonded dimer (b, transparent tubes show ionic interaction, hydrogens are omitted for clarity) and the comparison of the potential energy of interaction between the molecules in the dimer (c), estimated with GAFF and DFT, along with the distribution of the Zn-O bond length for the multi-molecular assemblies in the current study

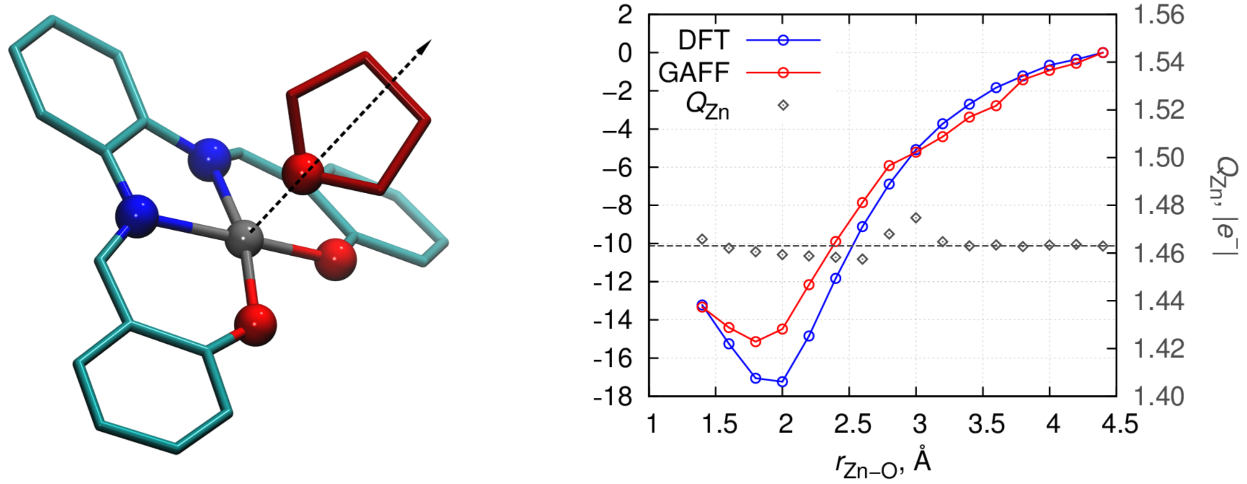

Figure S6 3D representation of mono-Zn(salphen) complex interacting with THF molecule (left) and the comparison of the profiles of potential energy of complex-solvent interaction (ΔU_{CS}) calculated with DFT (ONETEP) and GAFF (LAMMPS) at various (zinc)-(THF oxygen) distances $r_{\mathrm{Zn-O}}$ along with NBO estimated charge of zinc ion (Q_{Zn}) (right)

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