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## Supramolecular Metallacycles and their Binding of Fullerenes

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**Abstract:** The synthesis of a new triaminoguanidinium based ligand with three *tris*-chelating [NNO]-binding pockets and  $C_3$ -symmetry is described. The reaction of *tris*-(2-pyridinylene-*N*-oxide)triaminoguanidinium salts with zinc(II) formate leads to the formation of cyclic supramolecular coordination compounds which in solution bind fullerenes in their spherical cavities. The rapid encapsulation of  $C_{60}$  can be observed by NMR spectroscopy and single crystal X-ray diffraction and is verified using computations.

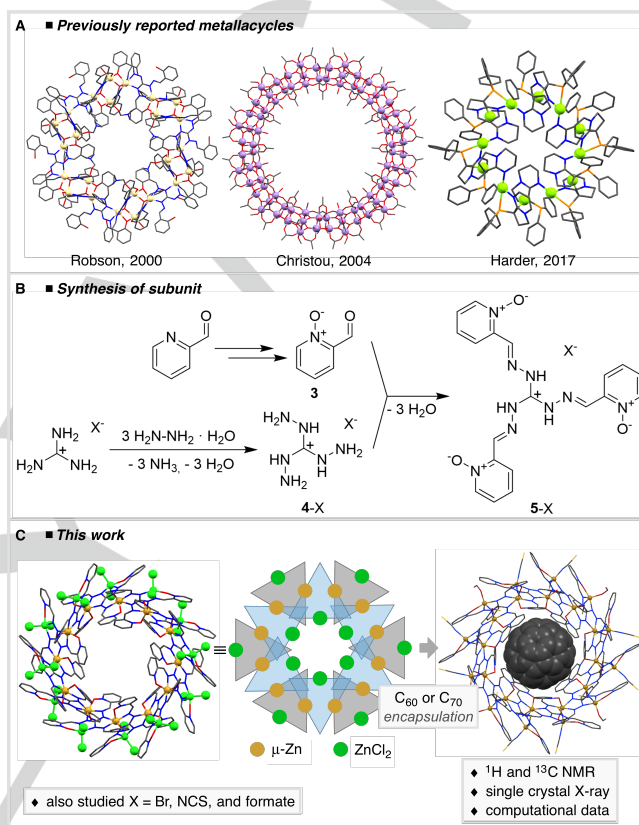
The development of supramolecular coordination compounds and their corresponding cages has attracted wide interest in recent years.<sup>[1]</sup> They have the potential to transport chemicals from one location to another in a specific manner, e.g. being used in drug delivery or as contrast agents.<sup>[2]</sup> The structural design of these containers requires precise and complementary building blocks but they are not limited to the incorporation of small organic molecules.<sup>[3]</sup> There are only a few examples of toroid coordination compounds and larger aggregates in the literature (Figure 1-A).<sup>[4]</sup> Those compounds can be used as single molecular magnets or in the separation of fullerenes.<sup>[5]</sup> Stang introduced the concept of using building blocks to form cage compounds<sup>[6]</sup> whereas the groups of Saalfrank, Fujita, and Nitschke used cages to stabilize reactive species like white phosphorous  $P_4$  and organometallic complexes.<sup>[7]</sup>

Toroids can be useful in binding guest molecules. Covalently bonded systems are quite common, e.g. cyclodextrins, cucurbituriles and cryptands which bind cations<sup>[8]</sup>, anions<sup>[9]</sup> or hydrophobic molecules<sup>[10]</sup> by variation of their peripheral decoration. Toroidal coordination cages are also able to bind guest molecules and separate fullerenes.<sup>[11]</sup>

These systems are challenging to model using density functional theory (DFT) due to their large size. Herein we demonstrate not only that a geometry-optimized structure of a large empty metallacycle can be obtained, but also the  $C_{60}$  and  $C_{70}$  encapsulated supramolecular entity. We were able to compute spectroscopic properties and assign the  $C_{60}$  signals in both the free state and bound inside of the metallacycle (Figure 1-C). There is a large number of studies reporting the computations of  $C_{60}$  itself. However, publications focusing on the interaction of  $C_{60}$  with other macrocycles are limited. Most studies including these interactions involve smaller, and often purely organic macrocyclic systems.<sup>[12]</sup> To the best of our knowledge, this is the first study to computationally investigate such large interacting systems (>4000 electrons) using non-truncated models.

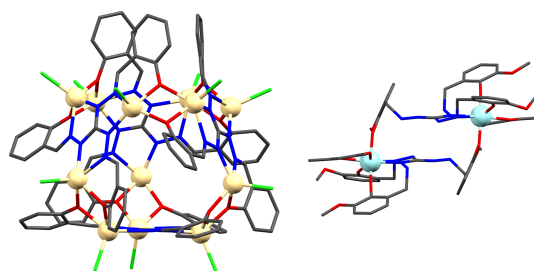
Our group demonstrated the synthesis of supramolecular structures by self-assembly of  $C_3$ -symmetric building blocks with three *tris*-chelating binding pockets and suitable co-ligands

(analogous to Figure 1-B).<sup>[13]</sup> Counter ions or solvent molecules typically serve as templates in the synthesis, so that discrete coordination cages like  $M_{12}L_4$  (Figure 2, left),  $M_{18}L_6$  or  $M_{24}L_8$  are accessible.<sup>[13d]</sup> We did not observe any activation of small molecules with these assemblies even though a high number of potential catalytically active metal centers are located proximal to each other.



**Figure 1:** (a) Previously reported supramolecular metallacycles. Hydrogen atoms and solvent molecules were omitted for clarity. Different scales were applied and metal ions highlighted as spheres. (b) Synthesis of the ligands  $[H_3(pyO)_3L]X$  (**5-X**), ( $X = Cl^-, NCS^-, BF_4^-$ ). (c) Supramolecular metallacycle  $[Zn_{24}Cl_{24}\{[H_3(pyO)_3L]_{12}\}]^{12}$  ( $ZnCl_2$  in green), schematic drawing and inclusion complex  $C_{60} \subset \mathbf{9}$ .

The overall negative charge of these complexes might be the reason why substrates like lactide are not satisfyingly activated. It was thus necessary to increase the amount of positive charges of the resulting coordination compounds by using stronger Lewis acids, such as  $Sn(IV)$  or  $Zr(IV)$ , instead of  $Cd(II)$  or  $Pd(II)$ .<sup>[14]</sup> The resulting complexes typically form dimers or trimers and are able to oligomerize acetone in up to 15 repeating units (Figure 2, right).<sup>[13d, 15]</sup>



**Figure 2:**  $M_{12}L_4$  tetrahedron and  $M_2L_2$  dimer ( $M = Cd, Sn$  respectively). Hydrogen atoms and solvent molecules were omitted for clarity.<sup>[14, 16]</sup>

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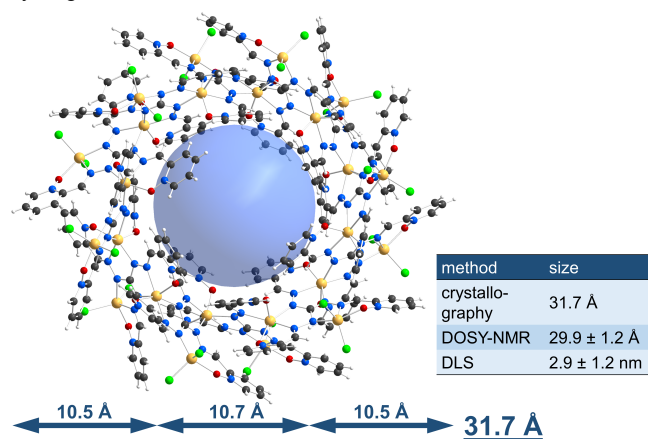
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In this work we address the charge issue by increasing the number of positive charges in the ligand itself, while maintaining the isoelectronic structure of the previously reported ligands. The ligand is prepared from a condensation reaction between 2-formylpyridine-*N*-oxide and the corresponding triaminoguanidinium salts TAG-Cl (**4-Cl**), TAG-NCS (**4-NCS**), or TAG-BF<sub>4</sub> (**4-BF<sub>4</sub>**), respectively (Figure 1-B).

The synthesis of *N*-oxide (**3**) requires standard protection and deprotection procedures for the aldehyde moiety. The oxidation of the pyridine nitrogen can be realized under mild conditions by using urea hydrogen peroxide with phthalic anhydride in acetonitrile.<sup>[17]</sup> Triaminoguanidinium salts (**4-X**) are obtained by the amination of guanidinium salts with hydrazine hydrate.<sup>[18]</sup> The resulting compounds (**5-X**) serve as an excellent ligands for Zn(II). The reaction of [H<sub>3</sub>(pyO)<sub>3</sub>L]Cl (**5-Cl**) with Zn(O<sub>2</sub>CH)<sub>2</sub> in *N,N*-dimethylformamide results in the formation of a supramolecular coordination compound [Zn<sub>24</sub>Cl<sub>24</sub>{(pyO)<sub>3</sub>L}<sub>12</sub>] (**6**, Figure 1-C) next to a coordination polymer of unknown composition. This torus-shaped metallacycle exhibits an outer diameter of 31.7 Å and Zn(II) ions are octahedrally coordinated between two alternately oriented ligands holding together the assembly (Figure 3 and Figure 4, left). The ZnCl<sub>2</sub> moieties occupy the remaining [NNO] binding pockets. A spherical cavity of 10.7 Å can be found inside the complex with a pore opening of 8.2 Å. Each value is corrected by the covalent radii of hydrogen or carbon atoms.

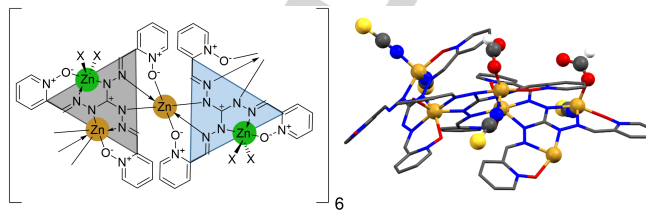


**Figure 3:** Molecular dimensions of metallacycles by X-ray diffraction compared to spectroscopic data of **7**. The void space is indicated by the blue sphere.

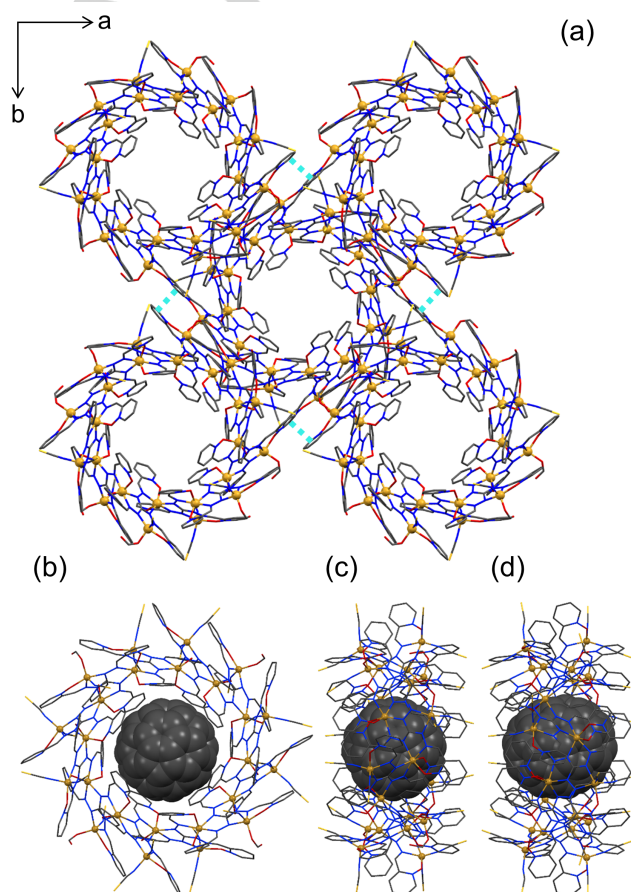
An isostructural cyclic coordination oligomer [Zn<sub>24</sub>Br<sub>24</sub>{(pyO)<sub>3</sub>L}<sub>12</sub>] (**7**) can be crystallized from the reaction mixture containing [H<sub>3</sub>(pyO)<sub>3</sub>L]BF<sub>4</sub>, ZnBr<sub>2</sub> and NaO<sub>2</sub>CH. DOSY-NMR (DMSO-*d*<sub>6</sub>) of **7** shows neither decomposition nor aggregation of the coordination complex in solution. Only one species is detected in addition to solvents and water. The diffusion coefficient of **7** is found to be  $D = (7.36 \pm 0.08) \cdot 10^7 \text{ cm}^2 \cdot \text{s}^{-1}$ . The hydrodynamic diameter of **7** can be determined to be 29.9 ± 1.2 Å using the Stokes-Einstein equation, which corresponds well with the observed diameter of the crystal structure (SI Figure 5-6).

Introduction of isothiocyanate leads to the formation of the analogous NCS-metallacycle [Zn<sub>24</sub>(NCS)<sub>16</sub>(O<sub>2</sub>CH)<sub>8</sub>{(pyO)<sub>3</sub>L}<sub>12</sub>] (**8**) with a 59 % yield. The zinc(II) ions, which were formally occupied by the halides Cl<sup>-</sup> or Br<sup>-</sup>, share those sites with isothiocyanate and formate co-ligands (Figure 4, right). The presence of this coordination compound, and the absence of smaller or larger aggregates in the DMSO solution, was confirmed by dynamic light scattering (Supporting Information). Since the co-ligands point outwards and exhibit a slightly increased steric demand, the system crystallizes in the

tetragonal space group P4<sub>2</sub>c with solvent filled channels along the crystallographic *c*-axis (Figure 5, a). Host-guest chemistry seems feasible since the cavities of the coordination oligomers should be accessible in the solid state. To our surprise, it was not possible to soak crystals of [Zn<sub>24</sub>(NCS)<sub>16</sub>(O<sub>2</sub>CH)<sub>8</sub>{(pyO)<sub>3</sub>L}<sub>12</sub>] (**8**) with a toluene solution of C<sub>60</sub>, as there was no observed color change.<sup>[19]</sup>



**Figure 4:** Schematic representation of metallacycles (X = Cl, Br, NCS, O<sub>2</sub>CH) and asymmetric unit of [Zn<sub>24</sub>(NCS)<sub>16</sub>(O<sub>2</sub>CH)<sub>8</sub>{(pyO)<sub>3</sub>L}<sub>12</sub>] **8**. Disordered solvent molecules were removed by the Squeeze routine (Platon) and hydrogen atoms were omitted for clarity.<sup>[20]</sup>

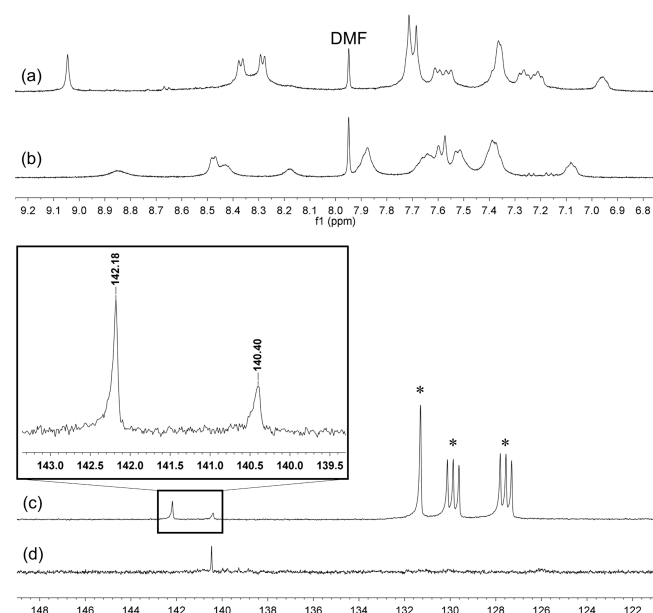


**Figure 5:** (a) Crystal packing of **8**,  $\pi$ - $\pi$ -interactions are highlighted in turquoise. (b, c) C<sub>60</sub>⊂**9**. (d) C<sub>70</sub>⊂**9**. Disordered solvent molecules were removed by the Squeeze routine and hydrogen atoms were omitted for clarity

From these experimental results we decided to encapsulate the fullerenes into the metallacycles in solution. A solution of empty metallacycle (**8**) was added to a toluene solution of C<sub>60</sub> or C<sub>70</sub>. Single crystals of the respective inclusion compounds were collected after a few days (Figure 5 b-d). The C<sub>60</sub> and C<sub>70</sub> are fully incorporated into the cavity of the metallacycle [Zn<sub>24</sub>(NCS)<sub>20</sub>(O<sub>2</sub>CH)<sub>4</sub>{(pyO)<sub>3</sub>L}<sub>12</sub>] (**9**). The lattice parameters underwent a slight change compared to **8** whereas

the space group was maintained. The periphery of the metallacycle was slightly perturbed, presumably due to the change in polarity of the solvent mixture.

The incorporation of  $C_{60}$  in solution is validated by NMR (Figure 6). Crystals of **8** and  $C_{60}$  were removed from the crystallization solution, washed with THF and dissolved in  $DMSO-d_6$ . The  $^1H$ -NMR spectrum shows a shift and broadening of the signals due to the molecular tumbling of  $C_{60}$ . The  $^{13}C$ -NMR of  $C_{60}$  shows only one signal for  $C_{60}$  which is in agreement of all carbon atoms being chemically and magnetically equivalent. The encapsulated  $C_{60}$  can only be detected next to free  $C_{60}$  in a highly diluted solvent mixture, and therefore  $^{13}C$  enriched  $C_{60}$  was used. The 2 ppm signal shift from 142.18 ppm (free  $C_{60}$ ) to 140.40 ppm ( $C_{60}$  in **8**) clearly indicates the incorporation of  $C_{60}$  in the cavity of the metallacycle.

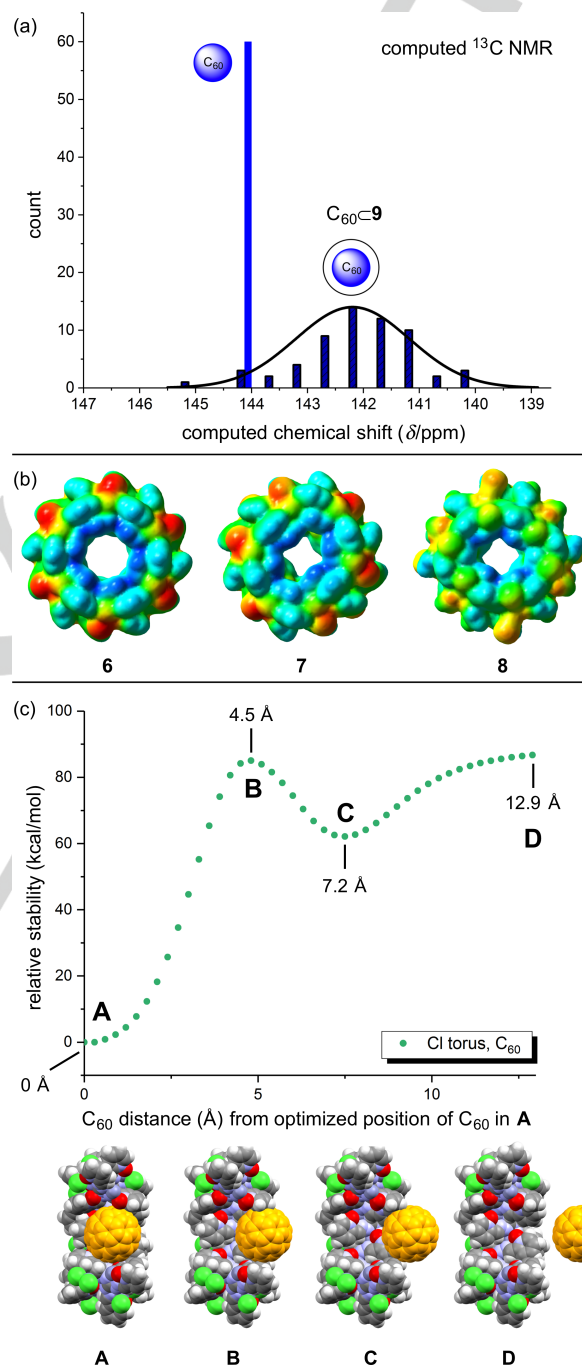


**Figure 6.** (a, b)  $^1H$ -NMR in  $DMSO-d_6$  of **8** and  $C_{60}$  respectively. (c)  $^{13}C$ -NMR of **8** (1 eq) and  $C_{60}$  (2 eq) in  $DMSO-d_6/1,2$ -dichlorobenzene- $d_4$  1:1 (v/v). (d)  $^{13}C$ -NMR of  $C_{60}$  in  $DMSO-d_6$ .

Calculations predicted the encapsulation of  $C_{60}$  by the metallacycle (**6**) to be favorable (Figure 7 c, **A**). However, there is an additional local minimum (**C**) where the  $C_{60}$  interacts with the periphery of the metallacycle. This has also been observed crystallographically. An analogous binding plot is observed for the  $C_{70}$  case (see SI for details). The use of dispersion corrections in these calculations is critical in order to correctly model the attractive interaction. In addition to the entropy loss, there is an electronic energy barrier (**B**) that  $C_{60}$  (and  $C_{70}$ ) must overcome caused by steric interactions between the  $C_{60/70}$  and pyridinyl groups located at the entrance of the metallacycle. Due to the nature of these calculations, stepwise single point calculations from the fully optimized state (**A**) were applied. The binding energetics are only qualitative. The differences in electrostatic potentials for **6-8** are shown in Figure 7 b. The chloride metallacycle has the largest positive inner core while the outside  $ZnCl_2$  moieties carry the negative potential. This is gradually attenuated in the series of **6** > **7** > **8** with **8** having the least positive inner core. These potentials might be useful in tuning the affinity and specificity for guest molecules.

In agreement with experimental data, spectroscopic assignments using computations (DFT, see SI for details) predict an approximately 2.0 ppm upfield shift for the

encapsulated  $C_{60}$  species vs. the free  $C_{60}$  (144.3 ppm vs. 142.2 ppm) (Figure 7 a). The IR-signatures of an empty chloride metallacycle (**6**) also match the computed IR spectrum and the fingerprint region contains several characteristic absorptions (Figure 25 in the SI).



**Figure 7.** (a) Computed  $^{13}C$ -NMR of **8** and  $C_{60}$  in **8**, (b) electrostatic potential maps (ESP) of **6**, **7**, and **8**. (c) An electronic energy diagram showing the relative stability ( $kcal\ mol^{-1}$ ) as a function of the  $C_{60}$  distance from its position in the fully optimized state (**A**) in  $C_{60}$  in **8**. The  $C_{60}$  is stepwise extruded.

### Summary

We report the synthesis of a new type of *tris*-chelating pyridine-*N*-oxide based ligands  $[H_3(pyO)_3L]X$ . Coordination of zinc(II) ions leads to structurally interesting cyclic coordination

oligomers which serve as hosts for fullerenes C<sub>60</sub> and C<sub>70</sub>. The inclusion of fullerenes was observed by single crystal X-ray diffractometry, NMR, and was validated using computations. These metallacycles are robust and show no sign of decomposition. Although computations on such large systems are challenging, we were able to model the C<sub>60</sub>/C<sub>70</sub> encapsulated metallacycles and even predict spectroscopic data, which are in strong agreement with the experimental results. Electrostatic potential maps reveal that the positive charges of the cavity cores can be tuned by the peripheral halide co-ligands. These computations help to provide a deeper understanding of host-guest interaction in these metallacycles. Similar computations will no doubt be useful for the rational design of host molecules with other cargo. In the future, these complexes could serve as container molecules transporting important cargo.<sup>[2f, 21]</sup>

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** cage compounds • fullerenes • host-guest-systems • self assembly • DFT calculations

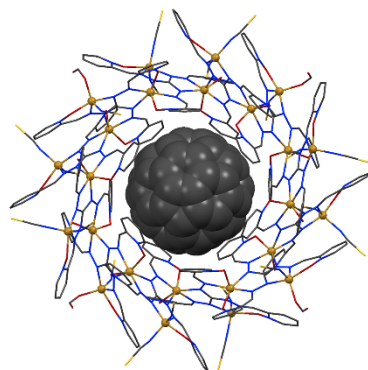
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## FULL PAPER

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