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Enhanced Gearing Fidelity Achieved Through Macrocyclization of a Solvated Molecular Spur Gear

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ABSTRACT: Molecular spur gear dynamics with high gearing fidelity can be achieved through a careful selection of constituent molecular components that favorably position and maintain the two gears in a meshed configuration. Here, we report the synthesis of a new macrocyclic molecular spur gear with a bibenzimidazole stator combined with a second naphthyl bis-gold-phosphine gold complex stator to place two 3-fold symmetric 9,10-diethynyl triptycene cogs at the optimal distance of 8.1 Å for gearing. Micro electron diffraction (μ ED) analysis confirmed the formation of the macrocyclic structure and the proper alignment of the triptycene cogs. Gearing dynamics in solution are predicted to be extremely fast and, in fact, were too fast



to be observed with variable-temperature ¹H NMR using CD_2Cl_2 as the solvent. A combination of molecular dynamics and metadynamics simulations predict that the barriers for gearing and slippage are ca. 4 kcal mol⁻¹ and ca. 9 kcal mol⁻¹, respectively. This system is characterized by enhanced gearing fidelity compared to the acyclic analog. This is achieved by rigidification of the structure, locking the two triptycenes in the preferred gearing distance and orientation.

INTRODUCTION

The beginning of nanoscience and nanotechnology can be traced back to 1959 when Richard Feynman gave his famous lecture, There's Plenty of Room at the Bottom, during which he challenged scientists and engineers to make a $(1/64)^3$ in³ operational electric motor.¹ Present day synthetic chemists are involved in making molecular and supramolecular entities with both structural and functional analogies to the macroscopic objects, including gears, pumps, and switches.² Early examples of molecular gears were published by Iwamura³ and Mislow⁴ in the 1980s, when they reported molecular bevel gear 1 (Figure 1), with two triptycenes covalently linked to a methylene group or an oxygen atom, respectively. In these landmark studies, they were able to show that the two triptycenes display fast and correlated dynamics, resembling those of macroscopic bevel gears. Since these pioneering studies, many triptycene-based bevel gears have been developed, including systems with three linear triptycenes⁵ or six cyclic triptycenes,⁶ switchable twogear systems,⁷ and a four-gear system with tunable dynamics.⁸ The study of molecular spur gears (MSG), with two gearing cogs arranged in parallel, has seen remarkably less success than its off-parallel counterparts.

Similar to the macroscopic objects, molecular gearing occurs when the two triptycenes undergo concerted, disrotatory motion, while slippage occurs either by conrotatory motion or independent rotation. As suggested by Siegel, the primary figure of merit for determining a gear's quality is gearing



Figure 1. Representative triptycene-based bevel (1), spur (2-6), and macrocyclic (6-7) gears. All spur gears arrange triptycenes in parallel while bevel gears position cogs at an off-parallel orientation.

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fidelity, which is defined as the number of geared rotations per slippage events $(F_{gear} = k_{gear}/k_{slip})$.⁹ Bevel gears with high gearing fidelity were developed utilizing tightly meshed systems in which the transition state leading to slippage was much higher in energy than the one leading to gearing (>30)kcal mol^{-1} vs 1–2 kcal mol^{-1}). Spur gears utilizing triptycene have strict geometric requirements to function properly, and there are no examples of structures shown to displayed high gearing fidelity. As discussed by Siegel and co-workers, the optimal distance for triptycene gearing is 8.1 Å, while the slippage transition state occurs at a distance of 7.2 Å between the rotational axes of the two gears. From this, the difficulty with achieving high-functioning spur gears becomes apparent, the transition state leading to slippage occurs at a shorter distance than does the one for gearing. This means that in order to have a properly functioning spur gear, stabilizing, enthalpic interactions must lower the energy of the gearing transition state to cause it to be favored over slippage. This issue is only exacerbated by the entropic penalty that arises as there are many rotational processes that can lead to slippage, while there is only one gearing trajectory.

Using a combination of molecular dynamics (MD) and quantum mechanical (QM) calculations, we recently explored the gearing and slippage trajectories in MSGs 2-5 (Figure 1).¹⁰ In this study, we discovered that divne-linked gears 2 and 4^{11} have calculated barriers of 5 kcal mol^{-1} for gearing and of 1-2kcal mol⁻¹ for slippage, respectively. Interestingly, the monoalkyne-linked gear 3 shows the inverse preference for gearing over slippage, which we attribute to the reduction in flexibility of 3 over 4 by having only a single alkynyl linker rather than two. Our calculations also showed that the flexibility of 5 might reduce its gearing efficiency, dropping the gearing barrier to 2.4 kcal mol⁻¹, which is quite close to that of slippage at 3.5 kcal mol^{-1} (down from 3.4 and 7.6 kcal mol⁻¹, respectively, when calculated with DFT). Clearly, when one considers the many different vibrational and torsional modes accessible to various MSGs rather than simply the transition state (TS) energies, a more complicated picture of gearing emerges. From this vein, the design of MSGs requires not only careful engineering of gearing and slippage barriers but also designing highly rigid structures where torsional degrees of freedom are limited to gearing processes.¹²

One method to reduce the number of degrees of freedom present in a linear or branched molecule is to convert it into a cyclic structure. This is particularly true for macrocyclization reactions, as evidenced by the need for templating agents to overcome the high entropic penalties present in their syntheses.¹³ While macrocyclic MSGs such as 6 and 7 from the Bryan¹⁴ and Toyota¹⁵ laboratories, respectively, have been developed, there was no systematic study of how the macrocyclization affects gearing efficiency in either case. We envisioned that locking the triptycene cogs into the proper orientation for gearing using a cyclic structure would restrict high amplitude bending modes that might reduce gearing efficiency or facilitate independent rotation of either triptycene, and ultimately enhance gearing fidelity. From this understanding, we sought to synthesize a new macrocyclic MSG and characterize its dynamics using a combination of molecular dynamics (MD) simulations and density functional theory (DFT) calculations. Our design utilizes 5, the bibenzimidazole stator developed by Siegel and co-workers, which places two triptycenes in parallel, 8 Å apart (Figure 2). We prepared 8a and its deuterated analogue $8b^{16}$ with two parallel ethynyl



Figure 2. Design of new macrocyclic MSG built with intermeshed triptycene blades held in place by a stator consisting of a bibenzimidazole and a gold-phosphine capping group.

groups to form the desired macrocycle by linking 8a/8b with digold complex 9.¹⁷ The use of deuterated gears was envisioned as a tool to simplify the ²H NMR spectrum by removing potential overlapping of aromatic signals from the two components of the stator. Our group's experience with gold complexes inspired us to bond the naphthyl diphosphine 9 to 8 via an Au¹⁺ coordination bond.¹⁸ Compound 9 was chosen as the 2,7-naphthyl substitution pattern to place the two phosphine groups 8.07 Å apart, a close fit for the idealized bibenzimidazole stator. Complexation with Au(I) conveniently coordinates alkyne and phosphine ligands at an angle of 180°, allowing for the construction of MSG 10a/b with the two triptycenes oriented in parallel and separated by ~8.1 Å.

RESULTS AND DISCUSSION

Synthesis and Electron Diffraction Structure. With the above design principles in mind, we set out to synthesize MSG **10a** (Scheme 1). Synthesis for **10a** started with 9,10-diethynyltriptycene **11a**, which was treated with 1 equiv of *n*-





BuLi followed by 1.15 equiv of triisopropylsilyl chloride at -78 °C. Subsequent overnight reflux followed by chromatographic separation resulted in the isolation of **12a** in 40% yield with the double protected and unprotected compounds recollected and used in proceeding reactions. Compound **12a** was then reacted with the boc-protected bibenzimidazole stator **13** using standard Sonogashira conditions to afford **14a** in 60% yield. Both boc-protecting groups could then be removed by treatment with a 1:10 mixture of trifluoroacetic acid (TFA) and dichloromethane (DCM). This crude mixture was reacted with an excess of 1-bromo-2-chloroethane in the presence of Cs₂CO₃ and THF at elevated temperatures. A short silica column was run on this mixture to remove any excess 1-bromo-2-chloroethane before reaction with TBAF in THF to yield macrocyclization precursor **8a**.

We discovered that removal of the boc- groups before TBAF was critical for maintaining a yield of 40% for these reactions. Presumably, the bibenzimidazole stator was decomposed by the presence of ammonium hydroxide in our TBAF solution if we attempted to deprotect the alkynes first. Finally, **8a** was dissolved in CH_2Cl_2 with a single drop of triethyl amine (TEA) and treated with 2 equiv of (dimethylthiol)gold(I) chloride to forge a covalently linked organogold template for macrocyclization.¹⁹ Dropwise addition of **9** dissolved in CH_2Cl_2 produced the macrocyclic MSG **10a** in 60% yield after subsequent workup and trituration of the crude product. Molecular spur gear **10b** was synthesized using the same procedure with deuterated samples of **11b**, which proceeded with similar yields.

Once the solvent had been removed, the solubility of 10a or 10b became severely limited in all explored solvents, even at elevated temperatures. Despite their very low solubility, spectral characterization was possible by ¹H NMR, FTIR, and HRMS (SI section), but we were not able to obtain ²H and ¹³C NMR data within reasonable acquisition times as a result of sensitivity differences of 9.65×10^{-3} (assuming 100%) labeling) and 1.76×10^{-4} (at natural abundance), respectively.²⁰ Although large enough single crystals for X-ray diffraction could not be obtained, we were able to grow microcrystals suitable for electron diffraction by slow evaporation of 10a from bromobenzene. Using continuousrotation electron diffraction, the structure was solved at 1.10 Å in space group $P2_1/n$.²¹ Analysis of the crystal structure (Figure 3A) reveals that the bibenzimidazole stator takes on a somewhat puckered and twisted shape that forces two connecting points for each alkyne to be ca. 7.74 Å apart rather than the expected ca. 8.10 Å for the planar structure. Gratifyingly, the distance between each triptycene bridgehead carbons are ca. 7.90 and 7.73 Å apart for the bibenzimidazole and phosphine side of the molecular, respectively. The two phosphines on the coordinated stator are approximately ca. 7.58 Å apart, and 0.15 Å closer together than on the bibenzimidazole stator. This short distance may account for the puckering observed on the bibenzimidazole. Interestingly, the tetrahedral geometry of the phosphines causes substantial stator twisting on the gold-coordinated side of the molecule (Figure 3B), which brings the two triptycenes slightly out of parallel alignment. Closer inspection of the triptycene cogs (Figure 3C) shows that one blade of the first triptycene neatly packs into the fold of the second one in a C_s symmetric arrangement, indicating that the two triptycenes can engage in configurations conducive to gearing. Additionally, analysis of the crystal packing revealed that multiple molecules of 10a



Figure 3. Crystal structure of 10a (A) face on with key distances measured, (B) side on showing the effects of utilizing tetrahedral phosphines as stators, and (C) space-filling model with the phosphine ligand and alkynes hidden to show alignment of the triptycenes. (D) Crystal packing of 10a with phenylenes on four intermeshed triptycenes highlighted.

arrange to intermesh their triptycene cogs (Figure 3D). This finding would likely preclude any solid-state dynamics and prompted us to focus solely on the solution-phased properties of **10a**.

Variable-Temperature NMR. The labeling of both triptycenes of the molecular spur gear with a suitable substituent, as indicated by a dot in two of the blades in Figure 4, results in desymmetrized rotators that lead to the



Figure 4. Distinct sets of rotational gearing cycles (I, II, and III) of labeled triptycenes following the disrotatory interconversion of isomers by a gearing mechanism. Slippage requires conrotation and interconverts among isomers of the three sets. Three possible slippage transitions are shown. Enantiomeric conformers are denoted with prime symbols. Figure adapted from ref 10.

formation of 18 different conformers (a-i') distributed in three distinct, isomeric cycles (I, II, and III).²² Close analysis of these cycles reveals that gearing cycles I and II are related by a mirror plane, and thus can be classified as *dl* isomers, while gearing cycle III has an internal mirror plane, leading to its classification as the meso cycle. Conformers within a single cycle can interconvert via a concerted, disrotatory (gearing) motion of each triptycene, while conrotatory rotation or independent rotation leads to slippage, interconverting the cycles. If gearing occurs with high fidelity, the time average solution NMR spectrum of an ideally labeled gear will reveal two sets of signals for each of the four triptycene protons in a 2:1 ratio that corresponds to isomers a-f and a'-f, and conformers g-i' in the meso cycle. In a situation where gearing fidelity is low, these isomeric cycles will interconvert, leading to a single set of four proton signals that represent the timeaveraged spectrum of all the individual conformers a-i'. The first experimental test of our design was aimed at exploring the dynamics of the blades by variable-temperature ¹H NMR, knowing that without proper labeling we can only ascertain whether rotational exchange between the three nonequivalent blade site occurs faster or slower than the NMR time scale. We expected to gain an additional insight into the energetics of the gearing and slippage processes by taking advantage of computational methods, which could eventually be used to decide the type(s) of substituents that could make the two cycles experimentally observable.

As shown in Figure 5, VT 1 H NMR measurements with MSG 10b were carried out in CD₂Cl₂ solutions with



Figure 5. Variable-temperature ¹H spectra of MSG 10b at temperatures ranging from 295 to 187 K. The α - and β -protons are marked with blue and red arrows, respectively. Signals indicated by the black arrow correspond to the phosphine ligand.

temperatures ranging from 295 to 187 K, which is close to the freezing point of the solvent and the limit for our spectrometer. Similar results obtained with **10a** between 298 and 212 K are shown included Figure SI26. Triptycene protons parallel to the axis of rotation and *ortho*- to the bridgehead carbon (α -protons) are labeled with blue arrows while protons *meta*- to the bridgehead carbon (β -protons) are indicated with red arrows. While the spectra are relatively complicated, chemical shift changes of both the triptycene α - and β -protons are easy to follow. The β -protons are highly shielded due to interactions with the neighboring triptycene blades and are easily identified by their coupling pattern as two sets of apparent triplets between 6.9 and 6.5 ppm. By comparison, the α -protons pointing toward the two different stator components occur as apparent doublets between 8.1 and 7.75 ppm. A number of changes were observed for the four triptycene blade signals. The β -protons observed at 6.60 ppm at 295 K shifted upfield by 32 Hz, while the signal at 6.87 ppm shifted upfield by only 8.7 Hz. In contrast to this asymmetric change, both α protons shifted upfield by approximately 40 Hz as the temperature was lowered within the same range. As the temperature is lowered, the downfield signal experiences a 40 Hz upfield shift, similar to the two α -protons and the upfield β proton. Notably, the phosphine phenyl groups that are marked with a black arrow start as two sets of complex signals, one at approximately 7.55 ppm and another around 7.65 ppm, and they both shift upfield and merge as the temperature reaches 187 K. A similar broadening for all signals suggests that there are no internal dynamic processes in the ¹H NMR time scale indicative of signal coalescence resulting from a slow site exchange. In fact, chemical shift changes might arise due to changes in the macrocycle structure, potentially mediated by hydrogen-bonding interaction between the bibenzidimazole stator and the α -protons in the triptycene gear with broadening caused by an increase in the viscosity of CD_2Cl_2 as it nears its freezing point (Figure SI27).

One may conclude from the above experimental observations that the rotational dynamics of MSG **10**, whether gearing or slippage, are determined by free energy barriers that are easy to surmount even at 187 K. However, it is possible that differences in chemical shifts in the three nonequivalent blade position of each triptycene gear are not enough to elicit a noticeable effect in the NMR spectra. A simple estimate of the conditions that are needed to make rotational dynamics observable in solution by VT NMR can be obtained by analyzing the combined effect of the activation energy (ΔG^{\ddagger}) and the difference in chemical shift between different exchange sites ($\Delta \nu$), on the observed coalescence temperature (T_C), as determined by the following equation²³

$$\Delta G^{\neq} = 4.55 \times 10^{-3} T_{c}^{*} (9.97 \times \log T_{c} - \log(500 \times \Delta \nu))$$

For coalescence to be experimentally observable near the temperature limit of ca. $Tc \approx 180$ K of CD_2Cl_2 , gearing dynamics would require activation free energy values (ΔG^{\ddagger}) in the range of ca. 8.5 to 5.5 kcal mol⁻¹ for chemical shift differences between exchange sites $(\Delta \nu)$ that differ from ca. 200 to 1500 Hz, respectively. This suggests that in addition to high barriers, different sites would require substantially different shielding environments $(\Delta \nu)$ for gearing cycles to be unambiguously detected by VT NMR. With this information at hand, we turned to density functional theory (DFT) and performed NMR calculations to obtain the isotropic shift values for hydrogen atoms of the three different triptycene blades. Calculated isotropic shielding values of the most stable gear structure revealed frequency variations in the range of 500 to 1500 Hz at a spectrometer frequency of 500 MHz, as the one used in our experiments (SI Table SI1). On the basis of these values, we can conclude that an experimentally measurable rotational barrier at or above 187 K would need activation free energies greater than ca. 7–8 kcal mol⁻¹. However, it should be noted that this result is not an

indication of gearing and/or slippage, as both can occur with high exchange rates over low barriers. In fact, for distinct gearing cycles to be experimentally observed in solution by VT ¹H NMR, it is not enough to have optimal gearing barriers, but it would be also essential that slippage has a barrier that is substantially higher than 7–8 kcal mol⁻¹ as lower values will interconvert structures of the two types of cycles with corresponding NMR time scale.

Computational Studies. To analyze gearing dynamics by computational methods,²⁴ we sought to assess how well the two triptycenes stay intermeshed in the macrocyclic architecture as compared to the half-open gear with a bibenzimidazole stator previously reported by Siegel et al.9 We performed molecular dynamics (MD) simulations at 300 K for 1 μ s for the two molecular gear systems immersed in a DCM solvent box and tracked the distances between the bridgehead carbons in intermeshed triptycenes. MD simulations were performed using the GPU code (pmemd.cuda)²⁵ of the AMBER 16 package.²⁶ Parameters for all nonmetal atoms were generated within the antechamber module using the general AMBER force field (gaff).²⁷ Parameters for the Au¹⁺ ions were generated using metal center parameter builder (MCPB.py).²⁸ Further computational details are described in the SI section and in a recent publication from our group.² Figure 6 depicts the range of distances that the intermeshed



Figure 6. Interaxle distances between bridgehead carbons in intermeshed triptycenes for half-open gear (green) and locked macrocyclic gear (blue) as simulated in DCM at 300 K. The distribution of interaxle distances is wider for the half-open gear systems.

triptycenes are able to explore while undergoing their correlated motion. Triptycenes in the half-open gear (colored in green) spanned the range of ca. 7.0 to 9.5 Å with two broad peaks observed at ca. 7.4 Å and ca. 8.2 Å consistent with distances that are favorable for the slippage and gearing transition states, respectively. Notably, more conformations were found at distances suitable for the slippage transition state than for gearing. The distance range between triptycenes in the macrocyclic gear (colored in blue) was smaller varying from ca. 7.0 Å to ca. 8.6 Å with the highest probability density observed at ca. 8.1 Å, which suggests that triptycenes undergo their dynamics at a distance that is expected to favor the transition state for gearing. These theoretical observations support the use of macrocyclization in order to keep triptycene gears tightly intermeshed as a strategy to enhance the gearing fidelity.

Having gained insight into the positive impact of macrocyclization on the gearing process, we performed MD simulations in the temperature range used in the VT-NMR experiments in dichloromethane, from 207 to 300 K. The simulations were run for 1 μ s to allow the system to visit all the energetically relevant configurations. Rotational trajectories were analyzed by tracing the motion of each triptycene gear via dihedral angle changes that vary from -180° to 180° . The dihedral angle for each triptycene is defined as the angle between the plane of the bibenzimidazole stator and the plane of one of the triptycene blades. For a meshed triptycene system undergoing correlated rotation, gearing is observed when dihedral angles associated with different triptycenes turn in opposite directions by 60°. The MD trajectories performed at 207 K for 1 μ s showed multiple gearing events (Figure 7A). Plotting the dihedral angle evolution in time shows that as one triptycene gear is changing its dihedral angle in one direction by 60°, the other simultaneously responds in the opposite direction, as required for geared rotation. As shown in the bottom frames in Figure 7, the extent of correlated behavior between the two gears can be appreciated by plotting one dihedral as a function of the other. At 207 K the occupied sites are consistent with the three symmetry-related ground state configurations achieved via gearing (Figure 7A, bottom frame). As the MD simulations temperature increases, more gearing events are observed. At 247 K (Figure 7B) and 300 K (Figure 7C), multiple symmetry-related gearing trajectories each offset by a ca. 60° are populated. Configurations outside the diagonal gearing trajectories indicate slippage events.

In order to evaluate the activation barrier to gearing and map the energy landscape, we utilized an accelerated sampling technique via well-tempered metadynamics simulations. Metadynamics simulation were performed using the NAMD 3.0 program.²⁹ The free energy surface was reconstructed as a function of the dihedral angles describing each triptycene (Figure 8A). By introducing a bias potential (or force) that acts on the selected variables, the potential mean force (PMF) plot along the chosen coordinates was generated (Figure 8B). The lowest energy trajectories match the ones obtained with MD simulations (Figure 7C) and indicate efficient gearing. The energy barriers for gearing and slippage were calculated to be ca. 4 kcal mol⁻¹ and ca. 9 kcal mol⁻¹, respectively. Notably, the energy barrier for gearing is smaller than the 7.3 kcal mol^{-1} barrier calculated by Siegel et al. for the half-open gear with bibenzimidazole stator in the gas phase.⁹ The slight asymmetry in the PMF plot is attributed to the asymmetric structure of the molecular spur gear and its twisted framework.

Similar metadynamics studies were previously done by our group on Siegel's half-open molecular spur gear with an ethenyl bridged bibenzimidazole stator. For that system, we confirmed low rotational barriers for gearing and slippage (2.4 and 3.5 kcal mol⁻¹, respectively) and showed perfectly symmetric PMF plot.¹⁰ We believe that the locking of triptycenes in a meshed configuration, at suitable interaxle distance for gearing, stabilizes the gearing transition state and allows the system to efficiently undergo gearing dynamics. These computational observations suggest that gearing dynamics are outside the experimental NMR time scales, and the calculated barriers for gearing and slippage are too low for the motion to be observed experimentally via phase isomer formation.



Figure 7. Dynamic simulations of triptycene gearing carried out for 1 μ s at (A) 207 K, (B) 247 K, and (C) at 300 K in a locked macrocyclic gear immersed in DCM solvent box. Different colors in each plot represent dihedral angle values for the two intermeshed triptycene gears. A gearing event is observed when a dihedral angle for each gear is changing by 60° in opposite directions. Correlated maps show how the two dihedral angles are simultaneously changing in opposite directions; as one dihedral is increasing, the other is simultaneously decreasing. As the simulation temperature increases, more correlated motion events are observed and more symmetry-related gearing trajectories are generated.



Figure 8. (A) Dihedral angles (atoms circled in red and blue) used to define triptycene rotation in the macrocyclic gear. (B) Potential mean force plot for triptycene rotation generated using well-tempered metadynamics simulations. The top-left to bottom-right diagonals represent the lowest energy trajectory for gearing, with dihedral angles changing in opposite directions. Energy scale is in kcal mol⁻¹.

CONCLUSIONS

Our results suggest that macrocyclization is a valuable strategy for enhancing gearing fidelity in molecular spur gear systems in solution by locking the triptycene cogs into the correct position and orientation for gearing. Using a convenient convergent synthesis, we were able to create a rigid organogold complex with triptycenes aligned in parallel and at a proper gearing distance. The MD simulations showed that macrocyclization prevents **10a** from accessing slippage transition states and reverses the preference for slippage observed with MSG **5** by limiting the bending modes that would otherwise be accessible to the gear. Metadynamics simulations of the energetic profile for gearing indicated that macrocyclization did not change the relative barriers of **10a** significantly as



Figure 9. Ground state and key transition states for **10***a*, and other triptycene-based spur gears, as well as key intermolecular interactions for tuning energetic barriers.

compared to those of the half-open gear 5. In the macrocyclic gear, the barriers for gearing and slippage were ca. 4 kcal mol^{-1} and ca. 9 kcal mol^{-1} , respectively, while in the half-open gear 5, as previously studied by Siegel et al., they were ca. 7.3 kcal mol^{-1} and ca. 11.6 kcal mol^{-1} , respectively. While bevel gears only required tight meshing to create experimentally visible dynamics, spur gears also require finely tuned energy barriers that bring the barrier to slippage above 11 kcal mol^{-1} such that the gearing dynamics will be observable in solution using variable-temperature NMR.

These findings suggest that future iterations of triptycenebased spur gears should utilize macrocyclic stators that position triptycenes ca. 8.1 Å apart in a rigid structure to prevent slippage, and then alter the slippage barrier using asymmetric triptycenes containing a combination of electron poor and electron rich phenylenes. In this system, favorable orbital interactions would stabilize the ground state and gearing transition state, but would be lost in the slippage

transition state (Figure 9), widening the energetic gap between gearing and slipping.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01885.

Spectroscopic characterization, diffraction data, and computational methods (PDF)

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Notes

The authors declare no competing financial interest.

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