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Interlocking molecular gear chains built on surfaces

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Abstract  
Periodic chains of molecular gears in which molecules couple with each other and rotate on surfaces have been previously explored by us theoretically using ab initio simulation tools. Based on the knowledge and experience gained about the interactions between neighboring molecular gears, we here explore the transmission of rotational motion and energy over larger distances, namely through a longer chain of gear-like passive “slave” molecules. Such microscopic gears exhibit quite different behaviors compared to rigid cogwheels in the macroscopic world, due to their structural flexibility affecting intermolecular interaction. Here, we investigate the capabilities of such gear chains and reveal the mechanisms of the transmission process in terms of both quantum-level density functional theory (DFT) and simple classical mechanics. We find that the transmission of rotation along gear chains depends strongly on the gear-gear distance: short distances can cause tilting of gears and even irregular “creep-then-jump” (or “stick-slip”) motion or expulsion of gears; long gear-gear distances cause weak coupling between gears, slipping and skipping. More importantly, for transmission of rotation at intermediate gear-gear distances, our modeling clearly exhibits the relative roles of several important factors: flexibility of gear arms, axles and supports, as well as resulting rotational delays, slippages, and thermal and other effects. These studies therefore allow better informed design of future molecular machine components involving motors, gears, axles, etc.  

Keywords: molecular machines; molecular gears; gear chains; correlated rotations; ab initio calculations; graphene  

Introduction  
Rotational molecules, ranging from single small molecules to larger nanoscale systems, have been explored widely in the past years due to their potential as molecular motors1-3, and further, in building up larger cooperating molecular machines.4-6 On one hand, molecular motors are expected to transfer external energy (the input, i.e. light1, 7, electricity8, 9, chemical energy10-12, etc.) to
unidirectional mechanical motion (the output), thus providing a driving force to run molecular machines such as a nanocar\textsuperscript{13-15}. On the other hand, there is still a lack of fundamental understanding that is required to achieve the molecular-scale control of mechanical devices operating at the nanoscale, analogous to the rigid gears/cogwheels in a macroscopic machine system.

In the past years, gear(wheel)-like molecules\textsuperscript{16}, self-locked single molecules\textsuperscript{17} or interlocking molecule networks\textsuperscript{18} on the nano/molecular scale have been reported; on the micrometer scale, a solid-state SiO\textsubscript{2} nano-gear with diameter of around 100 nm was fabricated on highly ordered pyrolytic graphite (HOPG)\textsuperscript{19}. The design of molecular gears is still a largely unexplored area at the current stage. In recent years, we have started investigating this important topic. In a recent publication\textsuperscript{20} we reported theoretical explorations of basic gear-gear interactions for relatively simple but widely relevant models of two kinds of molecular gears, viz. 3-tooth PF\textsubscript{3} molecules attached to a Cu(111) surface and multi-arm (5-tooth) molecular gears attached to a graphene sheet, such that externally powered “driver molecules” induce the rotation of passive “slave molecules”. These molecular gears were computationally simulated using periodic models with an infinite linear chain of alternating driver and slave gears, in which two driver molecules flank each slave molecule. This geometry allowed us to study in significant and useful detail how neighboring molecular gears interact and transmit rotation from one gear to the next. In the present work, we significantly extend those results to examine longer chains of passive slaves: this will illuminate the capabilities and necessary conditions to transmit rotation over longer distances through realistic assemblies of multiple slave gears.

In the present work, we theoretically examine longer chains consisting of the same molecular gears that we proposed previously\textsuperscript{20}. These model systems serve as generic examples that allow us to reach general conclusions valid for a much wider range of situations. We show here that such molecules can form interlocking finite one-dimensional chains or even two-dimensional networks of gears that can transmit rotational motion across multiple gears. Compared to macroscopic rigid gears, the softness (flexibility) of the molecular-scale gears, of their axles and of their supports can cause quite different behaviors, such as a “creep-then-jump” or “stick-slip” effect, as well as slipping and skipping. It is therefore important to analyze such behaviors in order to enable the future design and fabrication of effective molecular machines consisting of several linked subsystems such as molecular motors, gears, molecular drive axles, etc.

In our modeling, we focus on “low-speed” non-vibrational interactions between gears. The simulations do not include “motor” molecules that convert energy input into driving forces; instead, the rotation will be externally applied to “driver” molecules that can transmit this rotation to a chain or 2-D array of “slave” molecules whose behavior is then studied; our “driver” molecules are thus generic. As such, we are not attempting to model surface systems that might be realized experimentally exactly as modeled, since we are not including the many complications of a motor molecule: the focus is instead on computationally analyzing the nature and behavior of chains of molecular gears. Thus, this work is a theoretical investigation which aims to provide a general theoretical foundation for a variety of future experimental designs, not only for one particular experimental realization.

**Modeling and computational methods**

Our previous work\textsuperscript{20} proposed a 5-arm gear made of a carbon ring (the carbon ring is extended with appropriate chemical groups such as cyano and ethynyl groups or fluorine atoms) which can be
attached to a graphene sheet with an intermediate metal atom acting as the pivot between the gear C-ring and a graphene C-ring. This design was inspired by the structures of sandwich compounds that have been studied in organometallic chemistry for several decades. According to the 18-electron principle which provides stable chemical bonds (in particular the mechanism of the formation of ferrocene), the intermediate metal atoms in the gear systems cannot be arbitrarily chosen: manganese and its congeners in the Periodic Table have been proved to be the exclusively suitable intermediates for a 5-membered carbon ring to stand firmly but rotate freely on a graphene surface; similarly, here we prove that chromium, molybdenum and tungsten atoms should be adopted to support a 6-membered carbon ring (see part I of the Supplementary Information). Similar sandwich structures can also be found from experimental syntheses, such as benzene(cyclopentadienyl)manganese(I) and (η⁶-graphene)₂Cr₂⁸⁻⁻³⁰⁻⁻.

Using DFT calculations, we study the interlocking and rotation process between two or more such molecular gears (like those illustrated in Figure 1 later in the text) by imposing successive rotations on a “driver” molecule (at one end of the gear chain), in order to obtain resulting forces, torques and rotations on the other “slave” molecules of the chain driven by it. In the simulation, we start from an arbitrary “driver” orientation defined as 0˚ in Figure 1 or 2 (or any other similar cases): for this initial driver orientation, while the drivers are kept aligned and fixed, the slaves and the graphene sheet are fully relaxed, yielding negligible net forces and torques on all atoms and molecules. The drivers are then made to rotate stepwise in a smooth quasi-static motion, to simulate how actual motor molecules might rotate. We allow full relaxation of the slave molecules at each imposed driver rotation angle, such that the slaves can follow any appropriate energy-optimized pathway, including rotation, tilting, bending, slipping, breaking up, etc. (the internal driver structure remains rigid during its imposed rotation, so it can also represent other types of motor molecules with possibly different properties).

Specifically, the simulation process involves two steps for each driver orientation. In “step 1”, we manually rotate the driver molecule rigidly clockwise by 10˚ about its rotation axis (which is close to being above the center of a carbon ring of the graphene sheet and perpendicular to the sheet), while keeping the slave molecules fixed: this generates a strained unstable situation with non-zero forces and torques acting on the slave molecules. In “step 2”, we re-optimize the slave molecules while keeping the driver rigid and fixed at its 10˚ rotation geometry, resulting in again negligible net forces and torques. This 2-step process is repeated iteratively until the driver molecule reaches the rotation angle of 80˚ (larger than the 72˚ between the arms of a 5-arm gear), which covers the symmetry reduced range of rotations according to the 5-fold symmetry of the 5-arm gear (for 6-arm gears, it is 60˚). For more detailed descriptions, please see our previous work on the mechanisms of gear-gear interactions. The reason for choosing a rotation step of 10˚ instead of a value closely related to the 5-arm symmetry of the molecule such as 12˚ (360˚/5=72˚, 72˚/6=12˚) is twofold: first, there is an arbitrariness in favoring the 5-fold symmetry of the 5-arm molecules vs. the 6-fold symmetry of the graphene support; second – as shown later in the discussion part – the behavior of the slave molecules is actually asynchronous to the driver’s rotation, with significant angular delays and bending of the arms, so that a symmetry-linked 12˚ step value is not necessarily more meaningful.

Since the single molecules considered here show only moderate distortions during rotation, the approximation of taking the drivers as rigid bodies is reasonable. However, for a supramolecular system that is very flexible and contains many degrees of rotation and bending, this assumption
might significantly restrict the rotational motion pathways and the scenario would often be more complex.\textsuperscript{31}

The finite gear chains are examined by periodic slab calculations using the Vienna Ab-initio Simulation Package (VASP)\textsuperscript{32, 33}, within density functional theory (DFT), and applying the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{34}. Dispersion corrections due to van der Waals interaction were included according to Grimme\textsuperscript{35}.

To simulate the behavior of rotating multi-arm gears built on graphene sheets, the Brillouin zone was sampled by $2 \times 1 \times 1$ k-points for the structures shown in Figures 1, 2 and 3, and by $1 \times 1 \times 1$ k-points for the 2D networks reported in Figure 5. For all geometry optimizations, the projector-augmented wave (PAW) method\textsuperscript{36, 37} implemented in the VASP code was adopted, with a maximum 400eV cutoff for the plane-wave basis set.

**Results and discussion**

**Gear chains with one driver molecule and several slave molecules.** The largest shortcoming of PF$_3$ gears (attached to the Cu(111) surface in our prior work\textsuperscript{20}) is that they have only 3 cogs/arms. This makes the interlocking between gears too flexible and loose: skipping (i.e. jumping of arms past each other) is favored by the wide 120˚ gaps between their 3 arms, by the inherent softness of arm-arm interactions, by the flexibility of molecular arms, as well as by the thermal vibrations (unlike the case of hard metallic teeth in macroscopic gears). For reference, we first consider the shortest chain possible: a driver and a slave (unlike in our earlier work\textsuperscript{20}, here the slave is in contact with only one driver, not two). Compared to our earlier simulation results\textsuperscript{20} for the same gear-gear distance, we find that, if a slave is only coupled to a single driver instead of two, the weaker interlocking further increases the risk of skipping: with a single driver, the slave only manages to follow the driver until a driver orientation of about 30˚ before stopping further rotation, rather than 60˚ with two drivers (see Figure S1 in the Supplementary Information for illustration). This skipping severely limits the potential use of such 3-arm gears.

Most real applications will need more tightly coupled gears, especially when a longer chain of slave gears needs to be driven. To this end, we earlier designed multi-arm gears, using 5-membered carbon rings substituted with cyano groups (-CN) and their capability in transmitting rotation to adjacent gears has been investigated before.\textsuperscript{20} Those simulations were also conducted using alternating drivers and slaves in infinite periodic linear chains (like those of the PF$_3$ gears).

![Figure 1. Coupling of two adjacent molecular gears of 5-membered carbon rings with cyano (-CN) groups (driver and slave as marked). Each gear is attached to the graphene sheet with an intermediate](image)
manganese atom (blue) acting as pivot. The intermolecular distance is equal to $3a$ (where $a$ is the graphene lattice constant). The CN arms of the slave molecule are labelled A–E. The curved red arrows illustrate their (counterclockwise) rotation while black arrows indicate the (clockwise) rotation of the driver molecules. All molecules have one of their nitrogen atoms highlighted in red to emphasize the rotations. The three panels correspond to three orientations of the driver molecules: 0°, 30° and 60°, respectively, see text.

We again start with the case of 1 driver + 1 slave, as depicted in Figure 1, and will then build upon that simpler case to 1 driver + 1 slave + 1 slave + 1 slave, as depicted later in Figure 2. The gears are placed in close mutual distance (3 carbon rings apart on the graphene sheet, viz. 3 graphene lattice constants) in order to make the intermolecular interaction relatively strong. At closer intermolecular distances (such as 2 carbon rings apart) the graphene surface is computationally found to be torn up due to the excessively strong interaction; in that case, the molecules would not even be pushed apart to other sites, because the binding between the rotor, the metal atom and the graphene sheet is very robust.

Figure 1 shows that this 5-membered ring by itself can successfully drive a neighboring slave gear at an intermolecular distance of $3a$, i.e. 3 graphene lattice constants: the 5-arm slave gear can accomplish a rotation of $1/5$ of a full cycle and thus can complete the 360° rotation due to its $C_5$ symmetry. The simulation covers the driver’s rotation from 0° to 80° which guarantees that the slave has gone beyond 72° (1/5 of a full cycle); it also makes clear that a second and subsequent rotations through 72° can take place in this case (as we will show below, a larger spacing between gears may result in “skipping” and thus stopping of the slave gears’ cyclic rotation, which is manifest already in the first period before 72°). We find that the planes of the $C_5$ rings are tilted with respect to the graphene surface, and that the CN bonds are bent (upward or downward) due to the strong intermolecular interaction at this relatively close gear-gear separation, compared with the larger gear-gear separation modeled earlier\(^{20}\), which does not cause any observable tilting. The angles between the CN bonds and the graphene plane range from -10° to +35°: those CN bonds nearer to the driver are significantly bent upward by up to +35° and those on the other side are bent down toward the graphene plane by about -10°, as illustrated in the side view in later Figure 3(A).

![Figure 2](image_url)

**Figure 2.** Chain of four adjacent molecular gears of 5-membered carbon rings with cyano (-CN) groups in which the gear at one chain end acts as a driver, rotating clockwise as shown by black arrows, and the other three gears are slaves. The intermolecular distance is $3a$. Each gear is attached
to the graphene sheet with a central manganese atom (blue) acting as pivot. All molecules have one of their nitrogen atoms highlighted in red to emphasize the rotations.

We then elongated the chain by adding more slave gears and observed their behavior. Results for the case of a chain of 3 slave gears are shown in Figure 2 and movie M1. Similar to the 1-slave case of Figure 1, the 3-slave gears tilt and their CN bonds bend by about -10° to +30° (see also the side view in Figure 3(B)). We observe that, as the driver is rotated, the last slave gear (slave #3) undergoes almost no rotation at first, and then jumps suddenly soon after the driver reaches about 70°, so as to almost catch up with the driver: thus, slave #3 follows the driver with a "creep-then-jump" motion that is very similar to the "stick-slip" motion familiar in friction and earthquakes, for example. This type of motion also happens to a lesser extent for slave #2, while slave #1 shows a much reduced version of this motion by following the driver rotation more closely. Interestingly, we have never observed in this system that the slave gears escape rotating: it appears that the arms in this system cannot skip past each other, so any delayed rotations are caught up and compensated for later by larger forward jumps. (We also note that the "jump angle" 70° of slave #3 is close to 72°, which corresponds to a fifth of a full cycle, i.e. the repeat angle of a 5-arm gear; however, we argue below that there is no reason for the first jump to occur in general at or near the driver rotation of 72°, i.e. we believe this proximity to be a mere coincidence and actually to depend on the chain length, i.e. the number of gears in the chain.)

Figure 3. (A) and (B) give side views of the 60° rotation geometries in Figures 1 and 2, respectively, looking parallel to the surface and perpendicularly to the chains.
Figure 4. Induced rotation angles of the three slave gears #1, #2 and #3 due to the rotation of the driver gear in Figure 2. The intermolecular distance is $3a$. The imposed uniformly changing orientation of the driver gear is shown as the straight black line. The rotation of each slave is defined as the average of the rotations of its five carbon atoms projected onto the graphene surface, since these 3 gears are not parallel with the graphene surface and the individual arm intervals are twisted away from 72˚.

To better understand the observed creep-then-jump behavior, the calculated rotation angles are plotted in Figure 4 for each gear in this system: while the driver rotates smoothly by a constant 10˚ at each step (straight black line), the first slave gear (red line) increasingly lags behind the driver by 0 to ~15˚ until the driver reaches ~70˚, then jumps slightly ahead, thus reducing its lag again beyond ~70˚; the next slave gear (slave #2, blue line) greatly magnifies the lag of slave #1, while slave #3 (green line) accentuates it further, almost to the point of not rotating at all before the driver has reached ~70˚, but still jumping to almost catch up beyond 70˚. We see the same behavior repeating itself in the driver orientation range of ~70˚ to ~140˚, and then again after ~140˚. (The range from ~70˚ to ~140˚ again reminds us of the fifth-of-cycle angle of 72˚: in this case, we will argue that the repetition angle is indeed 72˚.)

Influence of gear-gear distance. Finite linear chains with a driver molecule on one end followed by a number of slave molecules (such as MnC$_5$(CN)$_5$ gears on graphene) were shown in the last section above to be capable of transmitting rotational motion. However, we also find sizable tilting of the gears, which leads to considerable potential barriers in rotation (up to about 0.3 eV, depending on the degree of tilting, compared with a barrier much smaller than 0.01 eV in the parallel/non-tilting case): these barriers cause irregular “creep-then-jump” or “stick-slip” motion. The tilting is attributed to the relatively small gear-gear distance equivalent to 3 carbon rings on the graphene sheet (viz. 3 graphene lattice constants). Whereas a smaller mutual distance can break up the graphene sheets due to the excessively strong intermolecular interaction, a larger mutual distance
will reduce the tilting due to weaker intermolecular interaction, but will also increase the risk of skipping between adjacent gears. Thus, the choice of different gear-gear distances needs to be examined carefully and designed rationally so as to reach an optimum situation where the gears can rotate as freely as possible (with small tilting angles and rotational barriers) but can also couple closely with each other.

By adopting different equivalent adsorption sites on the graphene lattice (with lattice constant \(a\)), gear chains can assume only discrete gear-gear distances; for instance, between the distances \(3a\) and \(4a\), only \(\sqrt{13}a\) (\(\sim 3.6a\)) is a possible gear-gear distance on the hexagonal graphene lattice (see Figures 1, 2 and 5 for illustration). For the case of 1 driver and 1 slave, the system with gear-gear distance \(3a\) has been described above (see Figure 1) and shows successful rotation but considerable tilting of the slaves. In contrast, for a gear-gear distance of \(4a\), our simulations show that the arrangement will lead to skipping between gears. However, for a gear-gear distance of \(\sqrt{13}a\), the chain yields both continuous rotation and negligible tilting of the slaves, making this geometry the most favorable among 2-gear chains (see also Figure S2 in the Supplementary Information for detailed simulation results).

An a priori surprising behavior occurs when we elongate the 2-gear \(\sqrt{13}a\) chain to 3 gears. While the slave in the 2-gear chain rotates smoothly with the driver (cf. Figure S2), both slaves in the 3-gear chain soon stop rotating (Figure 5(A)). Addition of the 2\(\text{nd}\) slave behind the 1\(\text{st}\) slave is sufficient to cause permanent sticking of both slaves once slave \(\#1\) has reached an almost fixed orientation such that two of its arms (C and D) are about equidistant to the driver center (cf. Figure 5(A)): Movie M2 in the Supplemental Information helps visualize this behavior. Even more surprising is that this behavior also occurs for the larger gear-gear distance \(4a\) (Figure 5(B)). In this case both slaves stop rotating even sooner, since the additional space between gears allows the driver to slip past slave \(\#1\) more easily; also the slaves adopt almost fixed orientations, due to the weaker driver-slave interactions at the larger separation. Results for the \(3a\) distance are not plotted as we already have more inclusive data (for 3-slave chains) in Figure 4: for the case of the 2-slave chain with \(3a\) gear-gear distance, the difference is that the lag in rotation and the jumping of the slaves are much smaller than those exhibited in the 3-slave case.
Figure 5. Rotation angles of two slave gears #1 and #2 in a 3-gear chain with two different gear-gear distances, due to smooth rotation of the driver gear (see the caption of Figure 4 for details). The gears are separated by (A) $\sqrt{13}a$ and (B) $4a$ ($a$ is the graphene lattice constant). The geometries at which the skipping between gears becomes most obvious are plotted in the insets: for (A) the skipping occurs by 90º, as denoted with the ellipse on the curves; for (B) the skipping occurs by 60º as denoted.

It is intuitively clear that the 2-slave case causes a larger resistance to rotation than the 1-slave case (and even more so the 3-slave case), by cumulating the rotational barriers of both slave molecules: this can roughly double the total rotational barrier which the system has to overcome. Adding even more slaves may magnify this effect further, but not necessarily to unlimited levels: each slave gear can adopt a different “out-of-phase” orientation, so that barriers do not necessarily add up “in phase”; also, more complex behavior can be envisaged for longer chains, such as caterpillar- or snake-like reptation whereby only one slave at a time passes over its barrier, causing a ripple effect that propagates down the chain.

<table>
<thead>
<tr>
<th>Gear-gear distance (unit: $a = $ lattice constant)</th>
<th>Number of slaves</th>
<th>Continuity of rotation</th>
<th>Tilting and bending effect</th>
<th>Rotational barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3a$</td>
<td>1</td>
<td>Yes</td>
<td>The arms on the interacting side bend by $+15^\circ$ to $+35^\circ$ and the carbon ring is almost not tilted. See figure 3(A).</td>
<td>$\sim 0.25$</td>
</tr>
<tr>
<td>$3a$</td>
<td>2</td>
<td>Yes</td>
<td>The arms bend strongly by $\sim +15^\circ$ to $+35^\circ$ on one side and by around $-10^\circ$ on the other</td>
<td>$\sim 0.3$</td>
</tr>
</tbody>
</table>
interacting side; the carbon rings tilt by $\pm 5^\circ$ to $\pm 30^\circ$ for different orientations. See figure 3(B).
of the molecules, especially of the last slave which is relatively free to tilt: the tilting makes the arms scrape against the graphene support, which has a bumpy corrugated surface with significant barriers to rotation of the arms. Therefore, the more tilted slaves jump abruptly over those graphene-induced barriers rather than co-rotating smoothly with the driver. This behavior is akin to the jerky stick-slip motion of chalk that screeches across a blackboard or of geologic faults that slide slowly between sudden earthquake events. The stick-slip behavior will also be a major contribution to energy dissipation during rotation, as the sudden jumps can easily excite vibrations in gears and support.

We see that the soft interaction, flexibility and tilting prevent transmitting the rotation rigidly and immediately through a long molecular gear chain. Instead, as the driver rotates, stress and distortion build up gradually along the chain, especially when slaves are blocked from rotating by the support due to tilting: this distortion is most clearly visible in Figure 2 at 60° in the form of lateral displacements of the slave gear centers from the underlying C₆-ring centers, as the slave gears are pushed aside by the force from the driver gear; this also implies tilting of the rotation axle away from the surface normal, as shown in Figure 3; in addition, there is some bending of the arms of the gears, both in and out of the plane of the molecule. The stress is thus more or less evenly distributed as elastic energy along the chain length. The accumulated tension is suddenly released when it has grown large enough to finally overcome the barrier for rotating the more distant slaves, as seen from the red curve (“Step 2”) of Figure 6: the gradually increasing total energy from around 20° to 70° and from around 90° to 140° reflects the accumulation of the stress as the slaves increasingly lag behind, while its sudden drops around 70° and 140° correspond to the jumps shown in Figure 4.

Figure 6. The total torque of slave #1 and the total energy of the whole 4-gear chain system shown in Figure 2. As detailed in the text, the simulation at each rotation angle consists of two steps: (1) rotate the driver clockwise by 10° while keeping all the slaves fixed – the black and blue curves indicate, respectively, the total energy of the full system and the total torque acting on slave #1 at
this step; (2) re-optimize all the slaves while fixing the driver at its rotated geometry (see red curve for the total energy).

As detailed in the *Modeling and computational methods* section, our stepwise quasi-static model imposes driving forces (which can be reflected by the torque) in the 1st step, followed in step 2 by full relaxation of the slaves. The energy difference between step 1 and step 2 can thus also indirectly reflect the strength of the driving forces: at most rotation angles (30°-170°), the difference in energy ranges from 0.29 to 0.85 eV (6.69 to 19.60 kcal/mol), much larger than that in the PF₃ gears (0.02 to 0.09 eV, or 0.43 to 2.11 kcal/mol)²⁰.

The torque analysis scheme proposed in our previous work³⁸ provides a very convenient and simple method to measure the rotation direction and rotation strength of rotor molecules: instead of a geometry optimization that involves many steps of self-consistent field (SCF) cycles, the Pulay forces obtained from a single-point SCF calculation can serve to estimate the rotational trend of the rotor molecule. The application to molecules of the classical-mechanics concept of torque is analogous to the common use of quantum-based forces and Newtonian mechanics in ab initio geometric optimization and in molecular dynamics³⁸. Taking as an example the 5-arm gear which can rotate about the manganese atom (the pivot), the total torque acting on this molecule (and thus inducing rotation) can be defined simply as:

\[ \vec{T} = \sum_i \vec{r}_i \times \vec{F}_i, \]

where \(i\) runs over all the atoms (10 C atoms and 5 N atoms) that constitute the rotor, \(\vec{F}_i\) is the Pulay force acting on atom \(i\), and \(\vec{r}_i\) is the corresponding vector from the pivot (the manganese atom) to the position of atom \(i\). In the present case, the effective torque component perpendicular to the graphene sheet is of most interest, while its other components lead to the tilting of the rotor. The first step of the 2-step process creates driving forces that can be observed only on the still-fixed slave #1: forces observed on the atoms of slave #2 and #3 at step 1 are almost zero in the present scheme, because they do not directly interact with the driver. However, such forces directly imposed on slave #1 can later (in step 2) be transformed to stresses that more evenly spread along the chain. Consequently, the strengths of such forces on slave #1 – and thus the effective torque they cause – are quite helpful for us to understand the strength of the direct driving force which is expected to affect the whole chain. This effective torque is plotted as the blue curve in Figure 6 and is shown to be positive at all rotation angles, implying a unidirectional counterclockwise rotation of slave #1. Its value ranges from 0.59 to 7.95 nN·nm, compared to 0.18 to 0.30 nN·nm in the PF₃ case²⁰, showing a several times stronger driving force. The shape of the torque curve also reflects the process of accumulating and releasing the stress: the torque on slave #1 grows to produce a larger stress and larger total energy, while the torque almost vanishes during the slave’s jumps.

With the revealed mechanism, the longer we make the chain, the harder it will be to transmit the driver rotation to the most distant slave gear: in the particular case of our model system, four or more slave gears will thus require an input driver rotation angle considerably larger than \(~70°\) to build up enough tension along the chain to make the most distant slave gears rotate; we expect the required input rotation to be roughly proportional to the chain length, as the elastic energy is spread out along the length of the chain but needs to exceed a critical value near the last gears. Nevertheless, our system has 72° rotational periodicity and this implies that subsequent rotational jumps (after the first one) will repeat themselves for every 72° of input driver rotation angle, as seen in Figure 4 for
the second jump. To be more precise, we observe in Figure 4 that the initial 70° or so of driver rotation induces and builds up an initial lag in the slave rotation: in this phase the driver pushes against the slaves which resist the slaves’ own first rotation barrier (partly due to the more distant slaves), causing the slave arms to bend under the applied force and torque and the slave rotation to lag increasingly behind that of the driver. After the initial 60° of driver rotation, the slaves start to yield and then jump suddenly over the barrier around 70°-80°. Then, in the range 80°-100°, the slaves still catch up to the driver orientation, but more slowly and gradually. The range from ~40° to ~100° is then seen to repeat itself almost identically as a second cycle (110°-170°), indicating that already by about 40° the system has adopted a periodically repeating rotation mode in which the initial lag is incorporated and maintained.

A deeper understanding of the strength of such intermolecular interactions needs an energy decomposition scheme\textsuperscript{39-41}, by which the intermolecular interaction can be decomposed into four contributions: the direct Coulomb interaction between the two unperturbed molecules, the Pauli repulsion between the overlapping electrons, the orbital interaction, and the van der Waals interaction. Many analyses on systems very similar to those investigated here have been reported previously\textsuperscript{20, 42, 43}, thus we do not perform the analogous calculations here.

**Other analogous cases: 6-arm gears and gear networks formed with them.** The studies illustrated in Figures 1 and 2 adopt 5-arm molecular gears; several 6-arm gears that have $C_6$ symmetry (and thus are more in accord with the $C_6$ symmetry of graphene) also transmit rotation well; since the 6-arm gears are found to behave very much like the 5-arm gears, we here focus on other aspects to expand our understanding. We start with the simple case of benzene rings substituted with 6 cyano (-CN) groups, modeled using periodic cells – each unit cell contains 1 driver and 1 slave and the gear chain contains alternating drivers and slaves, spaced $4a$ apart. We used chromium atoms as the pivots, as discussed in the *Modeling and computational methods* section. This simulation is a logical extension of our previous work\textsuperscript{20} that modeled an infinite chain consisting of alternating 5-arm drivers and slaves. As expected, the slaves keep pace with the rotating drivers at all rotation angles, as shown in Figure S3 in section IV of the Supplementary Information. We further modeled gears with longer arms: the behavior of the 6-carbon benzene ring substituted with 6 ethynyl (-C≡CH) groups\textsuperscript{44} and chromium pivot atoms was also studied using the same scheme. Results are shown in Figure S4. This gear has 6 arms with each arm being longer than the -CN arms in the former studies. Its performance is found to be similar to that of the $C_5$-based gear except that the longer ethynyl arms can bend tangentially relatively more during the rotation (the slave arms are often somewhat curved and the angles between them are not exactly 72°).
Figure 7. Two typical models of gear networks consisting of C₆(CN)₆ molecules, using $\sqrt{3}a$ gear-gear distances: (A) 1 driver at the center of the rectangular structure can directly drive 4 slaves. (B) 1 driver at one corner of the square structure can drive 3 slaves through two converging linkage paths. The purple atoms denote chromium atoms – the pivots of the 6-arm gears. Both (A) and (B) demonstrate the configuration of the gears at the driver orientation of 0°. See Figure S5 for the results at 20° and 40°.

Our main interest here is the behavior of finite non-periodic chains of such gears. Taking the C₆ symmetry into account, we adopt C₆(CN)₆ molecules to mesh into 2D networks consisting of 1 driver surrounded by 4 slaves (see Figure 7(A)), or 1 driver at the corner of a diamond and 3 slaves at its other corners (see Figure 7(B)). Such structures are commonly used in macroscopic gear systems existing in e.g. clockworks, gear boxes, etc. As demonstrated in Figure 7 (and Figure S5, for more details at the rotation angles of 20° and 40° of the drivers), these mesh structures function well: Figures 7(A) and S5(A) show that a single driver is able to drive another slave without skipping/slippage between their arms, and such 6-arm gears can be logically extended to finite gear chains like those shown in Figures 1 and 2; Figures 7(B) and S5(B) show that a driver at one corner can transmit its rotational motion to other gears via two paths (or even more, if needed), and this propagation can logistically be extended to larger 2D square or rectangular networks, based on the conclusions obtained from the aforementioned studies. We see that the slaves shown in Figures 7 and S5 are slightly shifted off their centers (the pivots, viz. the chromium atoms) due to the repulsion between the gears, but this does not hinder the gear-gear cooperation.

Conclusions
The present study, based on and extending our earlier work²⁰, investigates several prototypes of finite molecular gear chains. We show that gears with more arms couple better. Thus, the triple-arm gears studied in the previous work, such as PF₃ or NH₃ molecules attached to copper surfaces, are less effective in driving multiple slaves with only 1 driver, due to their sparse teeth. Multi-arm gears, e.g. 5-membered carbon rings substituted with 5 -CN groups or 6-membered carbon rings substituted with 6 -CN or 6 -C≡CH groups attached to graphene sheets, are better able to transmit rotation.
However, we also find that transmission of rotation beyond a few slave gears exhibits a “creep-then-jump” or “stick-slip” effect between gears, resulting both from soft and elastic interactions between and within gears, and from the scraping of tilted molecules against the supporting surface.

In the present work, we have modeled the cases of chains of 1 driver and 1, 2 and 3 slaves, as well as two extended 2D network models. For chains with more slaves the conclusion can be deduced logically: inasmuch as the gears are closely coupled (and thus skipping is prevented), the slave at the extremity of the chains can always follow the driver, even if with irregular rotation – as long as enough input driving force has been imposed. It is also noted that the assigned gear-gear distance can strongly influence the transmission of rotation, by affecting the strength of the intermolecular interaction and by generating the tilting of gears.

We note that a quasi-classical picture of these rotations is realistic and intuitive at a qualitative level: there is no need to invoke quantum mechanics to predict the general behavior of the gear rotation and gear-gear coupling. At the quantitative level, quantum effects clearly underlie these motions, e.g. for rotational and translational barrier heights, while quantum tunneling, thermal effects and energy dissipation will also have quantitative consequences.

Such studies can help designing gear systems which are indispensable in composing complicated machine systems, and may contribute to a blossoming of the development of nanoscale molecular robotics.

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Supporting Information Available
I. Stability of the 6-membered carbon ring supported by a chromium atom or its congeners;
II. limitation of the PF$_3$ gear: skipping (slippage) between arms of different gears in a finite gear chain;
III. the gear chain consisting of 1 driver and 1 slave with a gear-gear distance of $\sqrt{13}a$;
IV. 6-arm gears with chromium pivots;
V. 2D networks made with 6-arm gears;
VI. Movies of gear rotations within molecular chains of 3 and 2 slave molecules.

References
23. Rayón, V. M.; Frenking, G., Bis(benzene)chromium is a δ-bonded molecule and ferrocene is a π-bonded molecule. Organometallics 2003, 22, 3304.


