Supplementary Information

Interlocking molecular gear chains built on surfaces

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I. Stability of the 6-membered carbon ring supported by a chromium atom or its congeners

For structures explored here, each of which contains three parts (a graphene sheet, a metal atom, and a rotor made of a 6-membered carbon ring substituted with 6 -CN groups), the binding energy is defined as

$$\Delta E = E_{total} - E_{pivot} - E_{rotor} - E_{sub},$$

where E_{total} is the total energy of the supercell containing one layer of graphene, one rotor molecule and the intermediate metal pivot atom, E_{pivot} and E_{rotor} denote the total energies of an isolated metal atom and the isolated rotor molecule, respectively, and E_{sub} is the total energy of the isolated substrate. The binding energies of all sandwich structures were calculated using VASP and shown to be rather robust and comparable in structure with that of ferrocene, as listed in Table S1. All energies were obtained from relaxed geometries.

	d_1(Å)	d_2(Å)	ΔE (eV)
$C_5H_5 \cdot Fe \cdot C_5H_5$ (Ferrocene)	1.63	1.63	-12.56
$C_6(CN)_5 \cdot Cr \cdot$ Graphene	1.57	1.75	-9.77
$C_6(CN)_6 \cdot Mo \cdot$ Graphene	1.69	1.90	-10.94
$C_6(CN)_6 \cdot W \cdot$ Graphene	1.72	1.88	-12.26

Table S1 Interplanar distances and binding energies of several sandwich structures. d_1 denotes the perpendicular distance between the carbon ring plane and the metal atom, while for structures containing graphene, d_2 denotes the perpendicular distance between the metal atom and the graphene plane.

II. Limitation of the PF_3 gear: skipping (slippage) between arms of different gears in a finite gear chain

As shown in Figure S1, the slave gear in the case of a finite gear chain with only one driver and one slave stops rotating at the driver orientation of ~30˚, remains stationary until 60˚ and then, beyond 60˚, turns back to almost its initial orientation at 0˚.

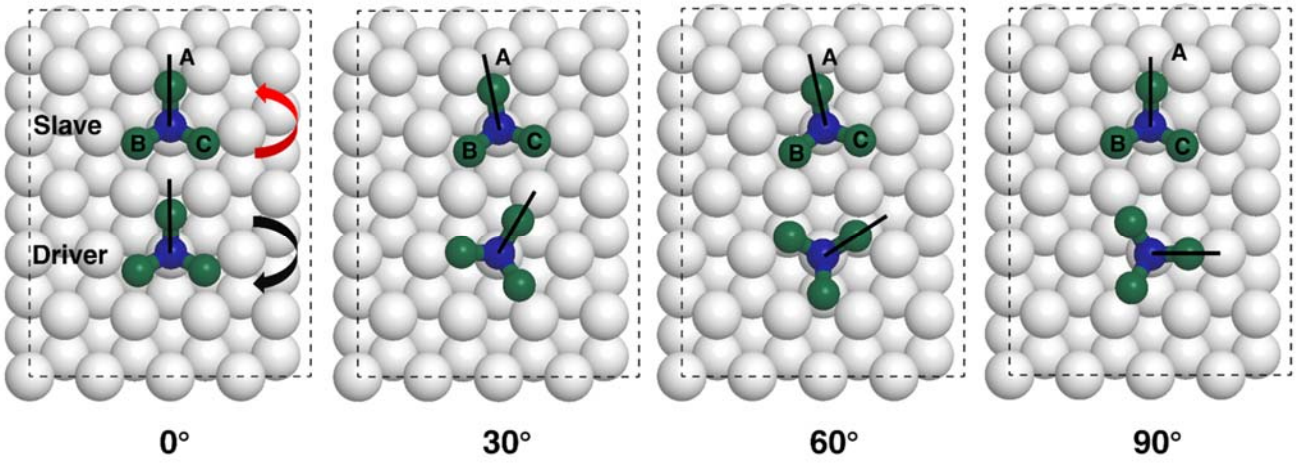

Figure S1 Calculated rotation (in top-down views) in a finite linear chain consisting of one driver and one slave PF_3 molecules (as labelled in the leftmost panel) on Cu(111). The slave (with arms labelled A, B, C) responds (as indicated by the curved red arrow) to the clockwise rotation of its driver PF_3 neighbors (as indicated by the curved black arrow). The four panels correspond to four orientations (marked by black bars) of the driver PF_3: 0˚, 30˚, 60˚ and 90˚, respectively. The gear-gear distance is $\sqrt{3}a$, where a is the Cu-Cu nearest neighbor distance at the substrate surface.

III. The gear chain consisting of 1 driver and 1 slave with a gear-gear distance of $\sqrt{13}a$

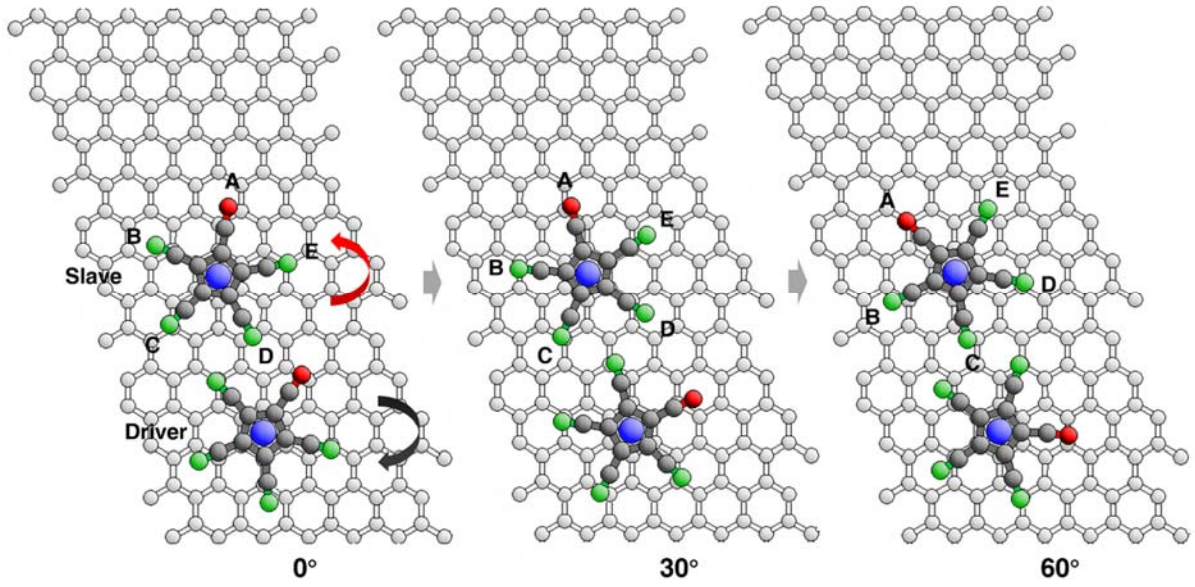

Figure S2 Coupling of two adjacent 5-arm molecular gears with gear-gear distance of $\sqrt{13}a$ (a is the graphene lattice constant). Each gear is attached to the graphene sheet with an intermediate manganese atom acting as pivot (blue). The CN arms of the slave molecule are labelled A-E. The curved red arrow illustrates their (counterclockwise) rotation while the black arrow indicates the (clockwise) rotation of the driver molecule. All molecules have one of their nitrogen atoms highlighted in red to illustrate the rotations. The three panels correspond to three orientations of the driver molecules: 0˚, 30˚ and 60˚, respectively.

IV. 6-arm gears with chromium pivots

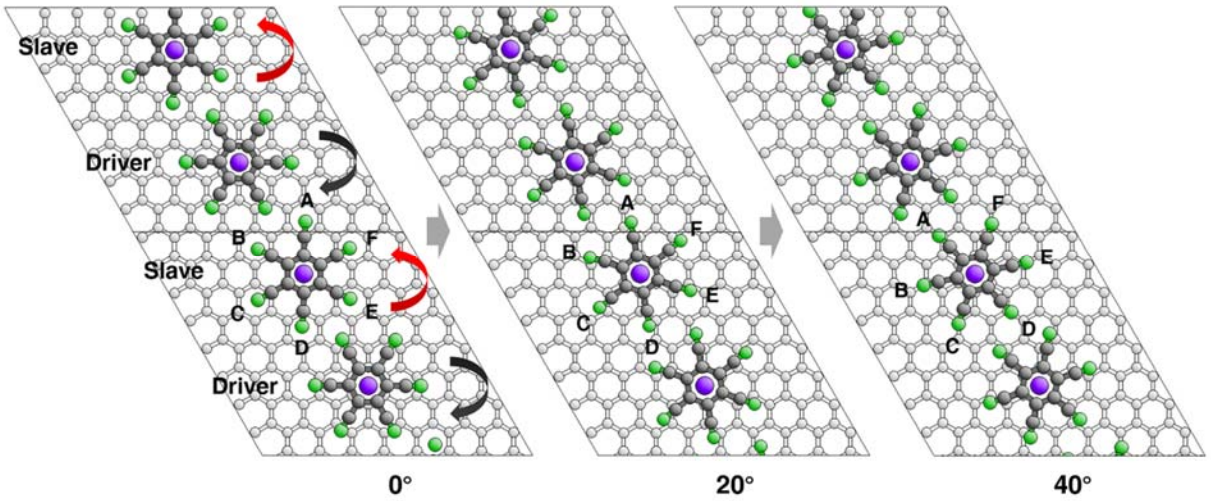

Figure S3 An infinite periodic chain of molecular gears (one driver and one slave per unit cell) consisting of 6-membered carbon rings with cyano groups (-CN). Each gear is attached to graphene with a central chromium atom (purple) acting as the pivot. The intermolecular distance is equal to 4*a*, i.e. 4 graphene lattice constants. The CN arms of a slave rotor molecule are labelled A-F. The curved red arrows illustrate the slaves' (counterclockwise) rotation while black arrows indicate the (clockwise) rotation of the driver molecules. The three panels correspond to three orientations of the driver molecules: 0˚, 20˚ and 40˚, respectively.

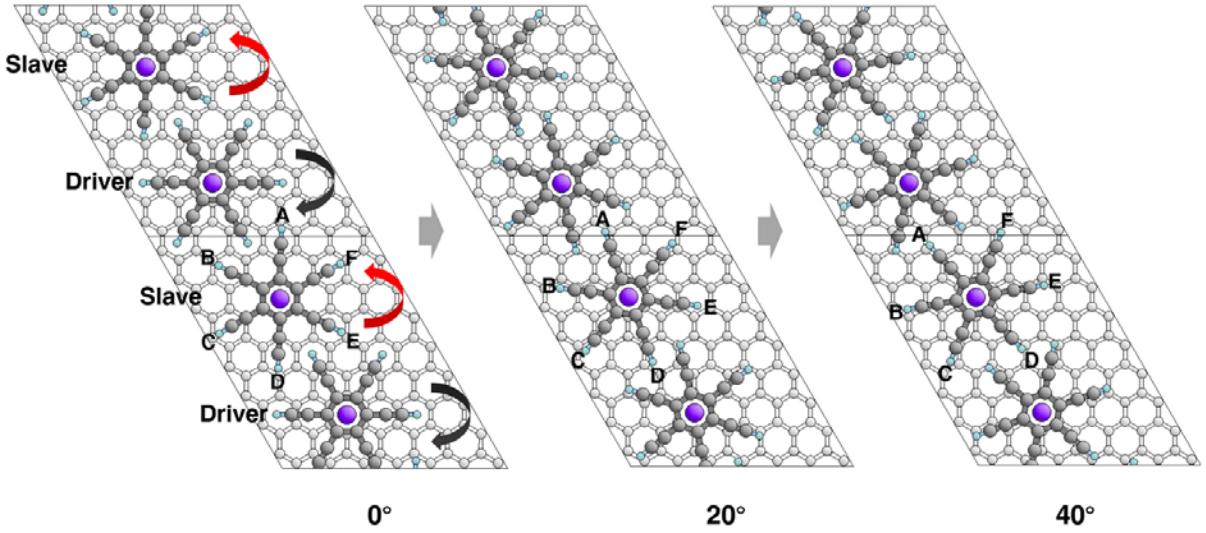

Figure S4 An infinite periodic chain of molecular gears (one driver and one slave per unit cell) consisting of 6-membered carbon rings with ethynyl groups (-C≡CH). Each gear is attached to graphene with a central chromium atom (purple) acting as the pivot. The intermolecular distance is equal to 4*a*, i.e. 4 graphene lattice constants. The C≡CH arms of a slave rotor molecule are labelled A-F. The curved red arrows illustrate their (counterclockwise) rotation while black arrows indicate the (clockwise) rotation of the driver molecules. The three panels correspond to three orientations of the driver molecules: 0˚, 20˚ and 40˚, respectively.

V. 2D networks made with 6-arm gears

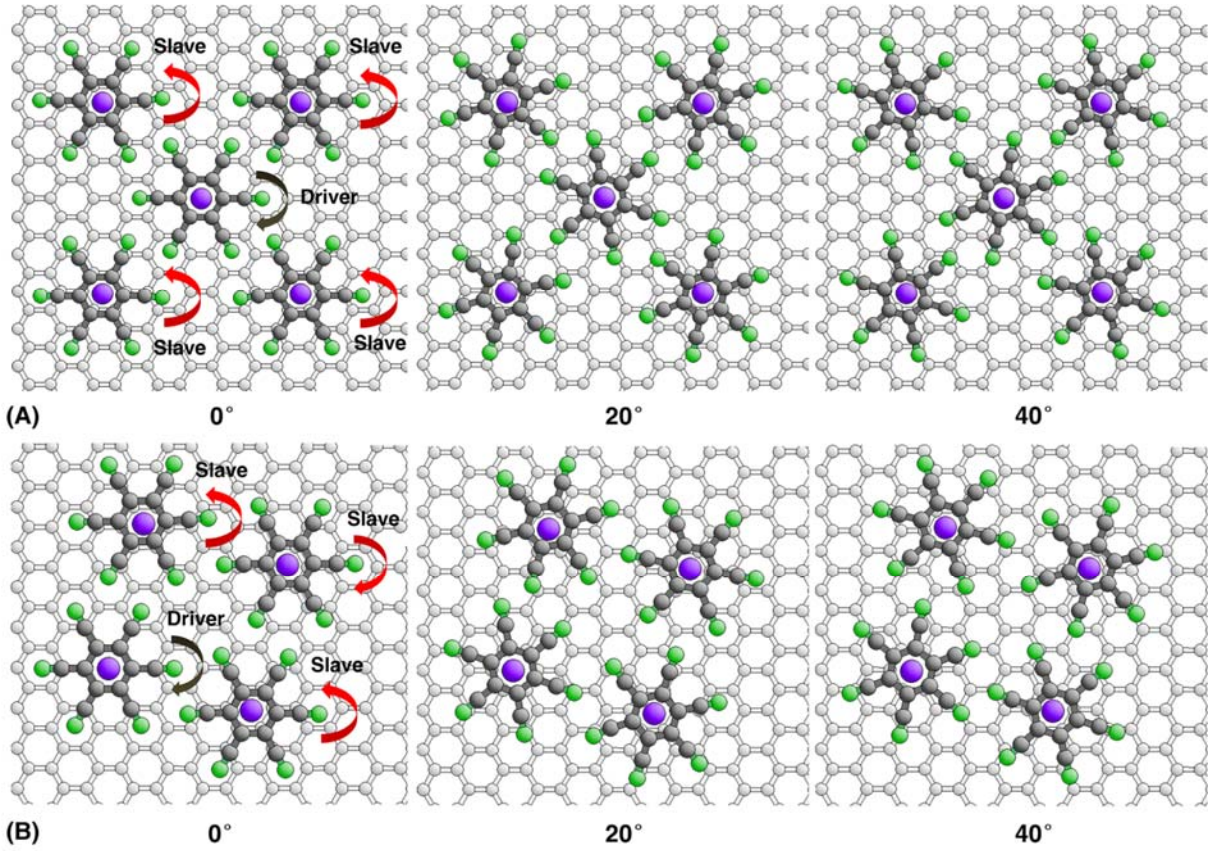

Figure S5 Two typical models of 2D gear networks corresponding to Figure 7, with $\sqrt{13}a$ gear-gear distances: (A) 1 driver at the center of the rectangular structure can directly drive 4 slaves. (B) 1 driver at one corner of the square structure can drive 3 slaves through two converging linkage paths. The curved black arrows illustrate the clockwise rotation of the driver while the red arrows indicate the corresponding counterclockwise or clockwise rotation of the slaves. The three panels in both (A) and (B) correspond to three orientations of the driver molecules: 0˚, 20˚ and 40˚, respectively.