

Synthesis of Regioisomeric Graphene Nanoribbon Junctions via Heteroprecursors

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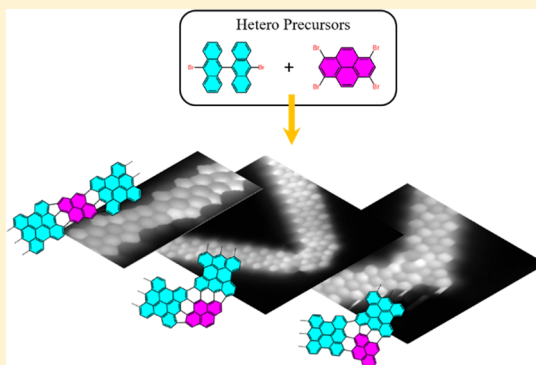
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Supporting Information

ABSTRACT: Graphene nanoribbons are one of the most promising materials for nanoscale electronics. While various structures have successfully been synthesized by on-surface reactions, curved connections remain less investigated, yet they could prove highly useful in the development of copolymerization technology. Here, we present the synthesis of three different regioisomeric junctions on Au (111) by using 10,10'-dibromo-9,9'-bianthryl and 1,3,6,8-tetrabromopyrene. The chemical structures and the electronic properties of junctions were studied with a combination of scanning tunneling microscopy with a CO terminated tip, scanning tunneling spectroscopy, and density functional theory calculations. We found that two identical nanoribbon-junction interface electronic states appear within the band gaps of connected graphene nanoribbons.



1. INTRODUCTION

Quasi-one dimensional graphene nanoribbons (GNRs) are considered as fundamental components for future carbon-based electronic devices due to their controllable electronic structures, which can be tuned by changing the ribbon width and edge structure. The so-called top-down approach, via the cutting of graphene and opening of carbon nanotubes, has demonstrated the possibilities of obtaining nanometer-sized GNRs.^{1,2} However, it is quite challenging to control their widths and edge structures at the atomic scale. In order to overcome this issue, a bottom-up approach, via on-surface synthesis, has been developed.³ In this technique, small molecules substituted by two halogen atoms are used as precursors. They are deposited on noble metal surfaces and then annealed to cleave the C–X (X = Cl, Br, I) bonds, and the resulting radicals then diffuse on the surface until stabilization by the formation of a C–C bond.³ Further annealing at higher temperatures induces the dehydrogenation of the polymerized chains, resulting in the formation of GNRs.⁴ With appropriate precursors, various GNRs with given structures have been synthesized, such as armchair edge GNRs with different widths,^{5–11} chevron GNRs,⁵ zigzag edge GNRs,¹² cove-edged GNRs,¹³ chiral GNRs,^{14–17} porous GNRs,¹⁸ and doped GNRs (B, N, O, S)^{19–26} as well as the

p–n and heterojunctions of GNRs.^{27–33} Among all the precursors, 10,10'-dibromo-9,9'-bianthryl (DBBA) is the mostly used even on different metal surfaces.^{34–36} For the future development of reliable electronic devices, it is of central importance to control the structure of junctions and investigate their electronic properties.^{27–33,37,38} Yet, structurally defined junctions between GNRs by a heteromolecule have not been demonstrated.

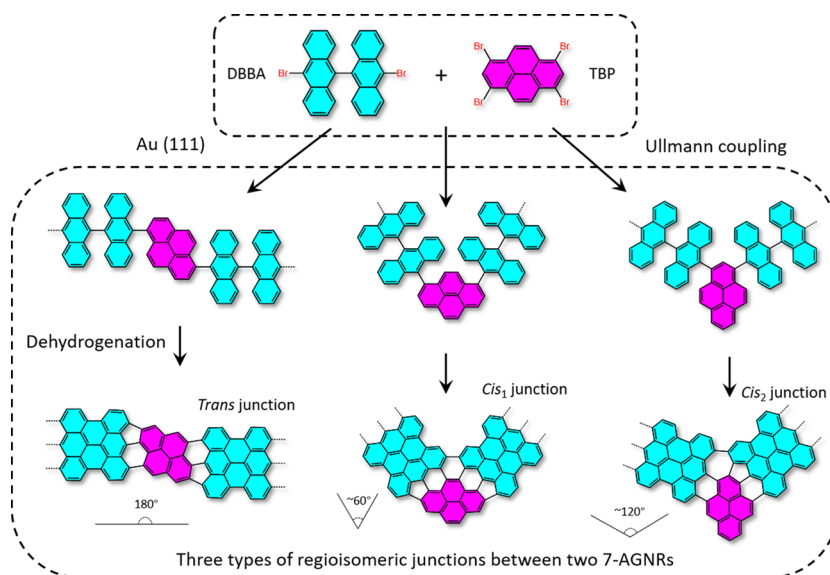
Here, we present the structural junctions of $n = 7$ armchair edge GNRs (n : the number of carbon in width), atomically defined by the backbone of 1,3,6,8-tetrabromopyrene (TBP) through an on-surface chemical reaction. When TBP reacted with DBBA on Au (111), TBP reacted with DBBA at two bromine sites out of four to give three different regioisomeric GNR junctions. Scanning tunneling microscopy (STM) with a CO functionalized tip shows the detailed structures of junctions. Furthermore, scanning tunneling spectroscopy (STS) revealed two local electronic states in the band gap of connected GNRs around the junction interface for each type of junction. Density functional theory (DFT)

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Scheme 1. Reaction Processes To Form Three Types of Regioisomeric Junctions between Two Graphene Nanoribbons



calculations also demonstrate the presence and character of these interface states. We propose that patterning GNR with regioisomeric junctions can lead to alternation of electronic properties of GNR.

2. METHODS

2.1. STM Measurements. All measurements were performed with a homemade low-temperature scanning tunneling microscopy (STM)/atomic force microscopy system, operated in ultrahigh vacuum at 4.3 K. The samples were prepared in an ultrahigh vacuum environment ($<5 \times 10^{-10}$ mbar). Au (111) surfaces were cleaned through cyclic sputtering (Ar^+ , 10 min) and annealing (750 K, 10 min). 10,10'-Dibromo-9,9'-bianthryl (DBBA, Sigma-Aldrich) and 1,3,6,8-tetrabromopyrene (TBP)³⁹ molecules were deposited with a ratio of DBBA to TBP of 10:1 onto the Au (111) surface held at room temperature. Then the samples were heated to 180 (15) and 320 °C (15 min) for dehalogenation and cyclodehydrogenation, respectively. The temperature of the sample was measured by a thermocouple and a pyrometer. A chemically etched tungsten tip was employed as a probe. For high-resolution imaging, the tip apex was terminated with a CO molecule, which was picked up from the surface.⁴⁰ The number of membered rings was determined by counting the number of neighboring rings as well as a void in the observed image. For constant height dI/dV imaging, the sample bias voltage was set close to zero voltage. The modulation amplitude was 7 mV_{rms}, and the frequency was 510 Hz. The WSxM software was used to analyze all measured images.⁴¹

2.2. Theoretical Calculations. All first-principles calculations in this work were performed using the periodic plane-wave basis VASP code^{42,43} implementing the spin-polarized density functional theory (DFT). To accurately include van der Waals interactions in this system, we used the optB86B + vdW-DF functional,^{44,45} selected based on previous work showing that it provides a sufficiently accurate description for all subsystems involved in the measurement. For similar systems,²³ this has given comparable accuracy in adsorbed molecular structures to vdW functionals D3⁴⁶ and TS.⁴⁷ For hybrid functional calculations, we used the HSE06 func-

tional^{48,49} along with the D3 method to include vdW contributions.⁴⁶

Projected augmented wave potentials were used to describe the core electrons,⁵⁰ with a kinetic energy cutoff of 550 eV (with PREC = accurate). Systematic k -point convergence was checked for all systems, with sampling chosen according to system size. This approach converged the total energy of all the systems to the order of meV. The properties of the bulk and surface of Au were carefully checked within this methodology, and excellent agreement was achieved with experiments. For calculations of the GNR junctions and GNR junctions on the surface, a vacuum gap of at least 1.5 nm was used, and the upper three layers of Au (five layers in total) and all atoms in the junction were allowed to relax to a force of less than 0.01 eV/Å.

For calculations of the *trans* junction, the size of the junction unit matched well to a gold supercell, but for the *cis₁* junction, the junction was reduced by 2% to find a reasonable match with gold. A comparison of the electronic structures of the original and reduced *cis₁* junctions showed no significant differences. STM images were calculated using the HIVE package⁵¹ based on the Tersoff–Hamann approximation.⁵² Atomic structure visualizations were made with the VMD package.⁵³

3. RESULTS AND DISCUSSION

We employ two kinds of precursor molecules (DBBA and TBP) to fabricate junctions (Scheme 1). If a small amount of TBP molecules is codeposited, DBBA molecules are expected to covalently connect to one of the four bromosubstituted sites in TBP via an Ullmann-type reaction. This conjugation repeats with DBBAs, resulting in the growth of a polyanthrylene attached to the pyrene core. Since TBP has four bromosubstituted sites, the position and the number of polyanthrylene units can vary. To simplify the discussion, here, we focus on junctions in which two polyanthrylene units link to one TBP. Subsequently, the cyclodehydrogenation induced by high-temperature annealing leads to the formation of a junction connecting two $n = 7$ GNRs. The angles between the GNRs at the junction, namely, 180, ~60, and ~120° (see Scheme 1),

define three types of regioisomeric junctions, that is, one *trans* and two *cis* forms, respectively.

Based on this scenario, we investigated reaction conditions for the construction of bis(polyanthrylene)-substituted pyrene as a major junction in on-surface polymerization. Fortunately, we found that when DBBA and TBP were deposited with a ratio of 10:1 onto a Au (111) surface at room temperature and heated at 180 °C, Ullmann couplings for DBBA-TBP conjugation as well as for DBBA polymerization proceeded smoothly to give the desired bis(polyanthrylene)-substituted pyrenes. Subsequently, the substrate was annealed at 320 °C to induce cyclodehydrogenation. Figure 1a shows the STM

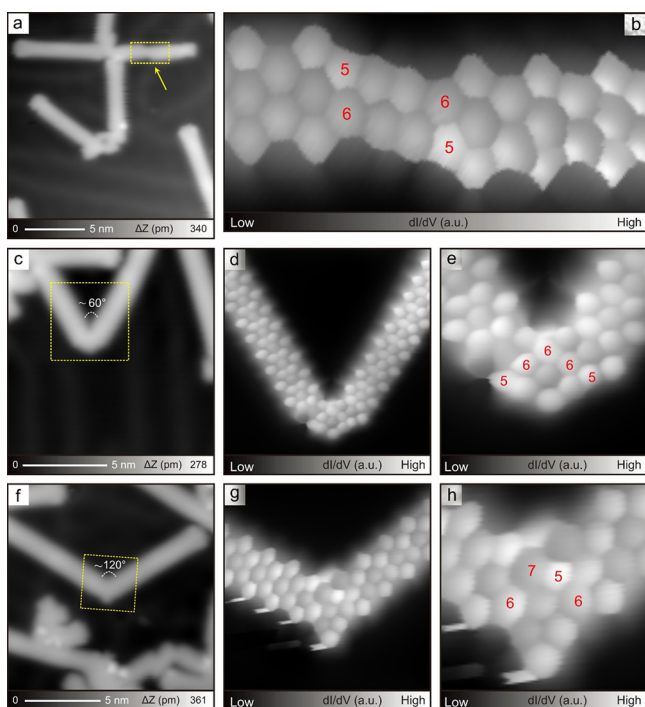


Figure 1. Three types of regioisomeric junctions synthesized on Au (111). (a) STM topography of a straight junction with a nodal site indicated by a yellow arrow. (b) CO terminated tip constant height dI/dV image of the area marked by a dashed box in panel (a). (c) STM topography of V-shaped junction with an angle of $\sim 60^\circ$. (d) Constant height dI/dV image of the area marked by a dashed box in panel (c) and its close-up view in panel (e). (f) STM topography of the V-shaped structure with an angle of $\sim 120^\circ$. (g) Constant height dI/dV image of the area marked by a dashed box in panel (f) and its close-up view in panel (h). Measurement parameters: Sample bias voltage $V = 200$ mV and tunneling current $I = 10$ pA in panels (a) and (f). $V = 200$ mV and $I = 5$ pA in panel (c).

topography in which a nodal site between two GNRs can be seen as indicated by a yellow dashed box. To investigate the structure in detail, the tip apex was terminated by a CO molecule.^{54,55} The lateral flexibility of the CO molecule on the metal tip ensures resolution of the inner structures of molecules on surfaces directly.⁵⁶ Figure 1b shows the detailed structure in which two GNRs are connected with a small offset along the longitudinal axis. At the center of the junction, four fused six-membered rings, corresponding to a pyrene core derived from TBP, can be seen. Therefore, the GNR is conjugated to TBP via one pair of five- and six-membered rings. This structure corresponds to a *trans* junction (Scheme

1). Note that the junction is chiral (Figure S1) and composed of zigzag edges.

We also found two types of *cis* junctions, which have both V-shaped structures. Figure 1c shows the STM topography of the junction with a narrower opening angle. The measured angle is about 60° , suggesting that it corresponds to a *cis*₁ junction. Indeed, the high-resolution dI/dV image shows the chemical structure in which two GNRs are connected symmetrically via TBP (Figure 1d). Figure 1e shows a close-up view of the junction in which two five-membered rings are indicated in red. Therefore, the GNR is connected to a TBP with one pair of five- and six-membered rings. Furthermore, a narrow gap between two GNRs results in the formation of a six-membered ring at the inner corner. From this investigation, it can be concluded that the structure corresponds to the *cis*₁ junction.

Figure 1f shows another example with a wider opening angle of $\sim 120^\circ$. A high-resolution dI/dV image taken around the area indicated by a dashed box in Figure 1f gives the detailed chemical structure (Figure 1g). The structure of the junction is not line symmetric as the GNR on the left-hand side is closer to the horizontal line of the image compared to the right-hand side. Figure 1h shows a close-up view of the junction in which asymmetric connections can clearly be seen. The GNR on the left-hand side connects to the TBP via one pair of six- and seven-membered rings, while the GNR on the right-hand side connects via one pair of five- and six-membered rings, matching the *cis*₂ junction (see Scheme 1). While we observed three types of junctions between two GNRs, junctions among three or four GNRs were not observed. It may be due to the fact that the steric effect between GNRs prevents the Ullmann-type reaction. On the other hand, one GNR terminated by TBP was observed (Figure S2). Note that observed junctions that are not defined by the backbone of TBP may relate to a random fusion of GNRs due to a low purity of the employed DBBA or C–H activation of the zigzag terminal of GNRs, as such junctions could also be seen without a TBP molecule (Figure S3).

Next, we investigated the electronic structures of the junctions by STS measurement. Figure 2a shows the STM topography of a *trans* junction on Au (111). The dI/dV curves were recorded above three different sites (Figure 2b), namely,

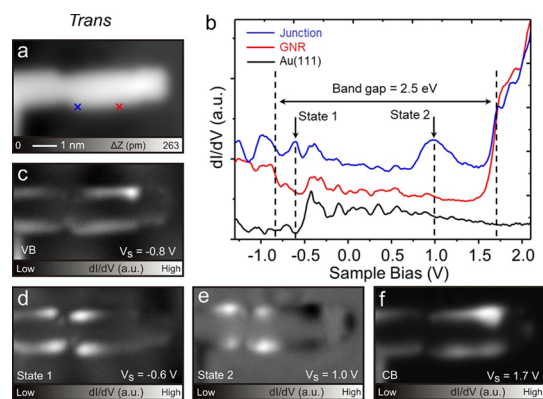


Figure 2. STS measurement of the *trans* junction. (a) STM topography of a *trans* junction on Au (111). (b) dI/dV curves were recorded at the junction (blue line) and bulk of GNR (red line) as well as Au (111) surface (black line). (c–f) A series of constant current dI/dV images were obtained at different sample bias voltages. Measurement parameters: $V = 200$ mV, $I = 10$ pA.

at the interface of the junction (indicated by a blue cross), at the bulk of the GNR connected junction (indicated by a red cross), and at the bare Au (111) surface as reference. The characteristic surface state of Au (111) at approximately -0.5 V is also visible in the dI/dV curves taken above the GNR and *trans* junction. Although the GNRs connect to the junction, no significant change of the valence band (VB) state (-0.8 V) and the conduction band (CB) state ($+1.7$ V) is observed above the GNR, remaining similar to an isolated GNR on Au (111).⁵⁷ Besides the VB and CB states, two additional peaks at -0.6 V and $+1.0$ V, marked by black arrows in Figure 2b, within the band gap of GNR can be identified. In order to investigate the spatial distribution of the electronic states, we took dI/dV maps at characteristic energies. Figure 2c,f shows the dI/dV maps at bias voltages of -0.8 and 1.7 V, respectively. The two additional peaks localize only in the close vicinity of the junction and disappear rapidly with the distance.

We also carried out STS measurement above two different sites of the *cis*₁ junction, indicated by crosses in Figure 3a.

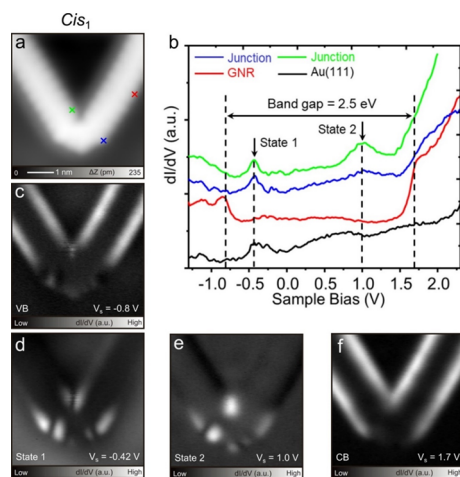


Figure 3. STS measurement of the *cis*₁ junction. (a) STM topography of *cis*₁ junction on Au (111). (b) dI/dV curves were recorded at the junction (blue and green lines), bulk of GNR (red line), and Au (111) surface (black line). (c–f) A series of constant current dI/dV images were taken at different bias voltages. Measurement parameters: $V = 200$ mV, $I = 10$ pA.

Figure 3b shows the corresponding dI/dV curves, and again, two additional peaks were measured at -0.42 and 1.0 V only above the junction (Figure 3b). Figure 3c,f shows that the VB and CB states of connected GNRs are distributed at the ribbon edges. The two interface states (-0.42 and 1.0 V) also localize in the vicinity of the *cis*₁ junction (Figure 3d,e), similar to the case of the *trans* junction. The electronic structure of the *cis*₂ junction was also investigated. The results can be seen in Figure S4 where two interface states (-0.56 and 0.87 V) are almost the same as those in *trans* and *cis*₁ junctions.

Three different junctions have been all synthesized through a single TBP molecule connecting terminals of two GNRs. Each of them introduces two localized states around the interfaces of junctions. This is of particular interest since interface states have the potential to tune the electronic properties of GNRs. For example, a periodic junction structure may introduce an interface state throughout the whole structure, resulting into a new band gap. Moreover, some periodic GNR junctions even have topological character.^{58–60}

In order to understand the origin and character of the observed interface states, we performed DFT calculations to study the atomic and electronic structures of the junctions. Since the observed properties were very similar for all the junctions considered, we focus here on the *trans* and *cis*₁ junctions. In Figure 4b, simulations demonstrate a clear presence of the state in the gap of GNR at about 0.5 eV and a further state at the top of the valence band at -0.5 eV. Calculated dI/dV maps at those energies (Figure 4c) show that they are dominated by states near the junction and show reasonable agreement with the equivalent experimental images (Figure 2). A more detailed analysis of the atomic character dominating states at those energies supports this, with carbon atoms around the junction playing a leading role (Figure S6).

Equivalently, for the *cis*₁ junction, Figure 5b shows that two clear states split off from the main GNR bands at about ± 0.3 eV, with characteristic features seen in the experimental dI/dV images (Figure 3) reproduced in the calculated maps (Figure 5c). As for the *trans* junction, these states are clearly dominated in character by carbon atoms at the junction (Figure S8).

Note that the electronic structure analysis presented in Figures 4 and 5 is based on isolated periodic junctions without the substrate for clarity, but we also simulated the same structures on a gold surface and obtained very similar results

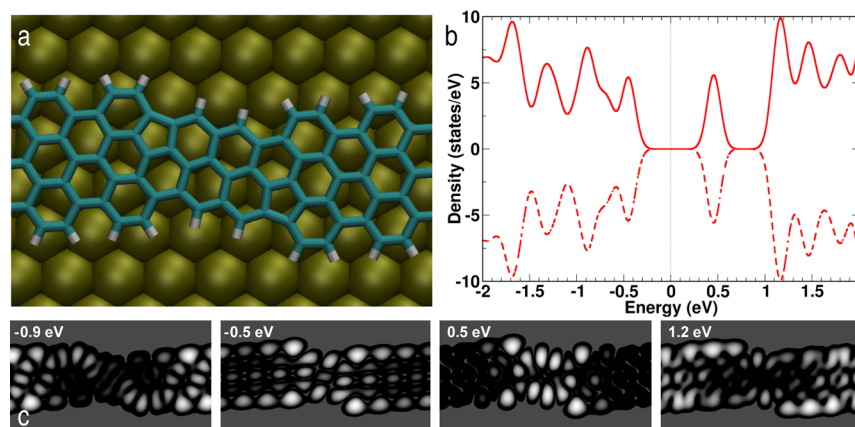


Figure 4. Simulated properties of *trans* junction: (a) atomic structure, (b) density of states around the Fermi energy where the solid line is spin up and dashed spin down, and (c) calculated dI/dV at a height of 0.3 nm above the junction and at the energies given.

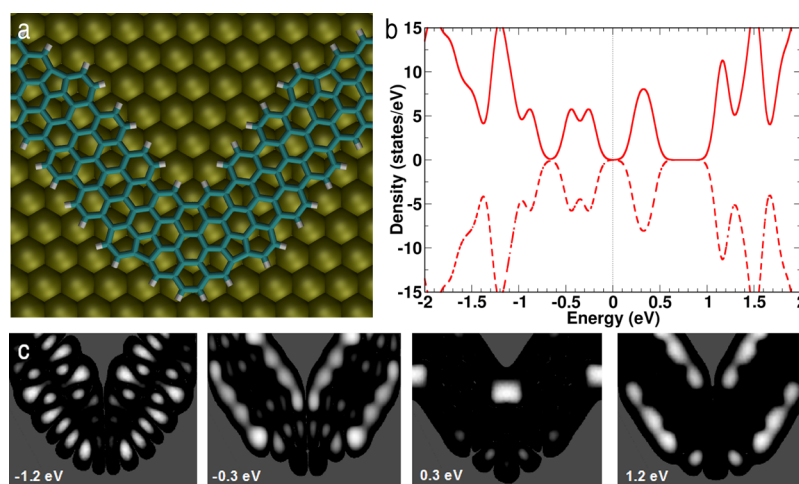


Figure 5. Simulated properties of *cis*₁ junction: (a) atomic structure, (b) density of states around the Fermi energy where the solid line is spin up and dashed spin down, and (c) calculated dI/dV at a height of 0.3 nm above the junction and at the energies given.

(see Figures S5–S8). Calculations of the junctions with hybrid functionals also demonstrated that the electronic structure is qualitatively the same and the interface states persist (see Figures S5 and S7).

4. CONCLUSIONS

By employing two heteroprecursor molecules, we have synthesized the structures of regioisomeric junctions between two $n = 7$ graphene nanoribbons by the backbone of a TBP molecule at the atomic scale. Since TBP has four Br substations, three possible connections were expected. Indeed, we found all three and characterized them by high-resolution STM and STS. GNRs and TBP molecules are conjugated with each other via five-, six-, and seven-membered rings, depending on the fused positions of the TBP. In contrast, the electronic structures of the three different junctions were almost identical. For all types, the nature of the effective defects creating the junctions means that the two interface states localize in their close vicinity. Since this technique offers a possibility to fabricate the structure of the junctions between GNRs, various junctions can be potentially synthesized. Thus, this finding may be a useful step forward toward carbon-based nanoelectronics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b05881.

STM images of chiral *trans* junctions, 7-AGNR terminated by one TBP or 7-AGNR, STS measurement of the *cis*₂ junction, simulated properties of *trans* and *cis*₁ junctions on the gold surface (PDF)

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Notes

The authors declare no competing financial interest.

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