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Regulation of quantum spin conversions in a single molecular radical

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Free radicals, generally formed through the cleavage of covalent electron-pair bonds, play an important role in diverse fields ranging from synthetic chemistry to spintronics and nonlinear optics. However, the characterization and regulation of the radical state at a single-molecule level face formidable challenges. Here we present the detection and sophisticated tuning of the open-shell character of individual diradicals with a donoracceptor structure via a sensitive single-molecule electrical approach. The radical is sandwiched between nanogapped graphene electrodes via covalent amide bonds to construct stable graphene-molecule-graphene single-molecule junctions. We measure the electrical conductance as a function of temperature and track the evolution of the closed-shell and open-shell electronic structures in real time, the open-shell triplet state being stabilized with increasing temperature. Furthermore, we tune the spin states by external stimuli, such as electrical and magnetic fields, and extract thermodynamic and kinetic parameters of the transition between closed-shell and open-shell states. Our findings provide insights into the evolution of single-molecule radicals under external stimuli, which may proof instrumental for the development of functional quantum spin-based molecular devices.

The development of devices based on the logic operation, storage, and information reading functions of electron spins has promoted the renewal of electronic information technologies¹⁻⁴. Currently, spintronic devices are facing dual demands of miniaturization and multi-functionalization, and there is thus an urgent need to develop sophisticated device processing technologies and expand material functions⁵⁻⁸. In comparison with traditional metal and inorganic

semiconductor materials, stable pure organic radicals are more promising candidates because of the weak spin-orbit coupling and hyperfine interaction of their light elements, enabling long spin coherence lifetimes⁹⁻¹¹. In addition, flexible molecular design and chemical synthesis endow the materials with multiple functions. However, the unpaired electrons predestine the radicals themselves to be highly reactive and short-lived^{12,13}, and the contact with metal electrodes further aggravates

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Single-radical molecular devices have been widely used in the study of the Kondo effect^{18,19}, magnetoresistance (MR) effect^{20,21}, entropy effect^{22,23} and spin filters^{24,25}, revealing the interaction between the unpaired electrons and conduction electrons at the molecular level. However, ensuring the stability and manipulating the spin of radical molecules at room temperature remains a challenge in developing single-radical molecular devices^{26,27}. In recent years, low-bandgap donor-acceptor (D-A) organic semiconductors have been reported to show universal open-shell diradical character in ground state²⁸⁻³¹. In comparison with the polycyclic aromatic hydrocarbons diradicaloids^{11,31}, these D-A diradicals exhibit the high photothermal and electrochemical stability under ambient conditions, and are potential candidates for spintronic materials. Notably, carbon-based (carbon nanotube and graphene) electrodes are compatible with organic molecules³² and efficiently avoid the destruction of intrinsic molecular properties through unique interface coupling due to chemical bonding^{18,33}. Moreover, studies on single-molecule photoswitches^{34,35}, intramolecular dynamics^{36,37} and reaction mechanisms^{38,39} based on graphene-molecule-graphene single-molecule junctions (GMG-SMJs) have been conducted. Changes in conductance signals due to cyclization, the stereoelectronic effect and bond formation/breaking are observed while the intrinsic properties of the molecule are maintained. The GMG-SMJ has proven to be an ideal scaffold for single-molecule devices measured at room temperature and can regulate spintronic properties.

In this Article, we report the detection of short-lived species of naphtho[1,2-c:5,6-c]bis([1,2,5]thiadiazole) derivative **NTCPhN** via a single-molecule electrical method, and the regulation of the evolutionary process of the electronic structures using heat and electric fields as well as magnetic fields. The functional centre of the molecular bridge has been shown to exist with small singlet–triplet energy splitting of the open-shell singlet and thermally accessible triplet state, thereby producing a relatively low singlet–triplet energy gap (ΔE_{ST})²⁸. The strong electric field generated by the applied bias voltage efficiently reduces ΔE_{ST} , and the external magnetic field interacts with the magnetic moments of unpaired electrons, providing strategies for the fast and reversible regulation of the open-shell quantum spin structures of diradical molecules.

Molecular synthesis and device preparation

The synthesis route and characterization of **NTCPhN** are shown in Supplementary Figs. 1–7. To provide a comparative analysis, we synthesized another closed-shell molecule **NTTPhN** (Supplementary Figs. 8–15), which shares a similar molecular structure with **NTCPhN**. Target molecules were integrated into the single-molecule platform through molecular engineering, utilizing well-developed methods for preparing of GMG-SMJs^{40,41}. Amino groups at both ends can chemically react with the carboxyl group at the end of graphene nanoelectrodes to construct a covalently connected interface, which endows the device with good stability and reliability. In addition, bulky side groups of the backbone can notably weaken π-stacking. Figure 1a is a schematic of a single-molecule device connected with **NTCPhN**, and the transformation of the electronic structures (Fig. 1b) can proceed under heating conditions²⁸. Further details on device fabrication procedures are presented in Methods and Supplementary Fig. 16. The success of the preparation of GMG-SMJs can be judged by the *I*-*V* curves showing a pathway state after molecular connection (Supplementary Fig. 17).

As shown in Fig. 1c, the single-electron transport behaviour of the device was observed, wherein the absence of Coulomb diamond overlapping indicates that only one molecule contributes to charge transport^{42,43}. Due to the difference in the capacitance coupling between the gate electrode and the molecule in different devices, some devices only exhibit a single or an incomplete Coulomb diamond (Supplementary Fig. 18). These devices, where the source-drain currents show the weak gate dependence, are attributed to a low gate coupling efficiency, rather than empty junctions or graphene nanoconstrictions⁴⁴. This is evidenced by the I-V measurements before and after molecular connection, revealing current levels of picoampere and nanoampere, respectively. Devices showing no obvious increase in current after molecular connection are eliminated in subsequent measurements. Moreover, the distinctive conductance states of NTCPhN, along with their characteristic behaviours under various bias voltages, temperatures and magnetic fields, are absent in graphene nanoconstrictions (vide infra). In addition, inelastic electron tunnelling spectroscopy shows that the specific molecular vibration modes match the theoretical calculations of infrared and Raman spectra (Fig. 1d, Supplementary Figs. 19 and 20, and Supplementary Note 1), again indicating successful device fabrication.

Temperature-dependent state conversion

Here, variable-temperature proton nuclear magnetic resonance (¹H-NMR) and ESR measurements were performed on a sample of **NTCPhN**. The ¹H-NMR spectrum has sharp and well-defined peaks at room temperature (Supplementary Fig. 21). When the temperature increased to 380 K, the onset of peak broadening was observed, indicating the population of a thermally accessible triplet state for **NTCPhN**⁴⁵. In addition, the ESR signals strengthened with an increase in temperature, which reveals the open-shell singlet ground state of **NTCPhN** (Fig. 2a). The SQUID measurement shows that the product of molar susceptibility and temperature ($\chi_M T$) increased with increasing temperature from 100 to 325 K (Fig. 2b). According to the Bleaney–Bowers equation, ΔE_{ST} obtained from the two experimental fits are close, being approximately–8.97 and –7.24 kJ mol⁻¹, suggesting the open-shell singlet ground state and thermally accessible triplet state of **NTCPhN**⁴⁶.

It is expected that the evolution of the electronic structure of diradical molecules with dynamic electrical signals can be obtained by taking advantage of the high temporal resolution and sensitivity of single-molecule electrical methods. To this end, real-time current (I-t) measurements (Fig. 2c) were made at different temperatures. In addition to the trend of an increasing current level, the evolution of the conductance states with increasing temperature is noteworthy. It was clear that the intermediate conductance state always dominated and could convert to high and low conductance states. However, there was no direct conversion between high and low conductance states. With an increase in temperature, the possibility of transformation from the intermediate conductance state to the high and low conductance states increased, and the transformation rate increased. As the temperature rose to 340 K, the high conductance state almost disappeared. According to Fig. 2c, we plotted the current distribution histograms of the 10-s I-t data and performed Gaussian fitting (Fig. 2d, top). The ratio of the area of each Gaussian peak to the total area reflects the proportion of the corresponding conductance state. As the temperature increased, the proportion of low and high conductance states exhibited an increasing trend, and the disappearance of the high conductance state at 340 K may be due to its short lifetime limited by the instrumental sampling rate. Furthermore, we used Qub software⁴⁷ to perform multi-level fitting on the current signals (Supplementary Fig. 22), and fitted the average lifetime of each conductance state using a single-exponential decay function (Supplementary Fig. 23)

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Fig. 1|Single-molecule device structure and molecular characterization. a, Schematic of GMG-SMJs connecting NTCPhN, omitting the dodecyl groups. Black, blue, red and yellow spheres represent carbon, nitrogen, oxygen and sulfur atoms, respectively. b, Resonant structural transitions between the closed-shell and open-shell forms of NTCPhN. c, Current stability diagram as a function of source-drain bias voltage (V_d) and gate voltage (V_g) of a device connected

with NTCPhN measured at 2 K. d, Experimental inelastic electron tunnelling spectroscopy (plotted using Bezier curves) measured by a lock-in secondharmonic technique at 2.0 K with an AC modulation of 10 mV (r.m.s. value) at a frequency of 331 Hz, and theoretically calculated infrared (IR) and Raman spectra. AC, alternating current; r.m.s., root mean square.

or arithmetic mean (when the number of conductance state conversions is too small), as shown in Fig. 2d. In contrast, the average lifetime of the intermediate conductance state was the longest, and that of the low conductance state was the shortest.

In addition, the transmission spectra corresponding to different electronic structures of NTCPhN were calculated, as shown in Fig. 2e. It is clearly seen that the transmission coefficient of the open-shell singlet structure is greater than that of the closed-shell structure in the energy range of -0.5 to +0.5 eV, which theoretically proves the feasibility of using the single-molecule electrical monitoring platform to detect short-lived species of diradicals. It is noted that the open-shell triplet state, which is an excited state with higher Gibbs energy, is not observed in our transport simulation and automatically converges to the open-shell singlet state. Moreover, the Gibbs free energy (ΔG) was calculated for the singlet and triplet states at different temperatures and found to change less with temperature (Supplementary Table 1). However, according to the Boltzmann distribution, even if ΔE_{ST} remains unchanged, the population of the triplet state (with higher energy) itself would be greater at higher temperatures.

Based on the resonant structures depicted in Fig. 1b, a qualitative understanding of the open-shell nature of NTCPhN can be obtained. The closed-shell singlet state corresponds to an electronic configuration with all electrons paired, resulting in a net spin of zero. Conversely, the open-shell structure possesses two unpaired electrons, as confirmed by ESR and SQUID measurements, with the spin-antiparallel configuration corresponding to the open-shell singlet state and the spin-parallel configuration corresponding to the open-shell triplet state. Among these structures, the closed-shell singlet state exhibits the lowest energy and the highest stability^{28,29}. Because the proportion of the conductance states reflects the stability of the corresponding states, the intermediate conductance state with an absolute dominance should correspond to the closed-shell singlet state. As for the open-shell states, the fitted $\Delta E_{\rm ST}$ values are negative, indicating that the open-shell singlet state is more stable than the open-shell triplet state^{28,46}. Considering the fact that the proportion of the high conductance state is higher than that of the low conductance state at low temperatures and the fact that the transmission coefficient of the open-shell singlet state is greater than that of the closed-shell singlet state, we infer that the high and low conductance states correspond to the open-shell singlet and triplet states of NTCPhN, respectively.

According to the transition direction of conductance state 2, τ_{21} (time of transition to conductance state 1) and τ_{23} (time of transition to conductance state 3) at different temperatures were fitted separately, and the rate constant $k = 1/\tau$ for each transition process was calculated, where τ is the average lifetime. By plotting a scatter plot of lnk versus 1,000/T at different temperatures and performing linear fit



Fig. 2 | **Temperature-dependent measurements and signal attributions. a**, Variable-temperature ESR spectra measured from 100 to 300 K with an interval of 20 K, the inset shows *IT* (*I*: integrated ESR intensity; *T*: temperature) versus *T*. **b**, SQUID magnetometry of the solid sample showing magnetic susceptibility times temperature $\chi_{M}T$ versus *T* in the range 100–330 K, fitted using the Bleaney–Bowers equation with g = 2.003. **c**, *I*–*t* curves (top) and corresponding enlarged *I*–*t* curves (bottom, grey) of the device at different temperatures with a

 V_d of 0.1 V. Conductance states 1, 2 and 3 are designated as red, blue and yellow, respectively. **d**, Gaussian peak and average lifetime for each conductance state in **c**. **e**, Transmission spectra of closed- and open-shell singlet structures. **f**.**g**, Arrhenius plots of the closed-shell singlet and open-shell triplet (**f**)/singlet (**g**) structural transition with temperature. E_a values were obtained by fitting the rate constants at the various temperatures using $\ln k = -\frac{E_a}{RT} + C$. The error bars indicate the 1 σ confidence interval of a single-exponential fitting.

(Fig. 2f,g), the activation energies (E_a) of the transition between different electronic structures can be obtained using the Arrhenius equation. E_a for the forward and reverse transitions from the open-shell triplet state to the closed-shell singlet state is $E_{1\rightarrow 2} = 42.0 \pm 5.0$ kJ mol⁻¹ and $E_{2\rightarrow 1} = 36.3 \pm 13.3$ kJ mol⁻¹, respectively. E_a for forward and reverse

transitions from the open-shell singlet state to the closed-shell singlet state is $E_{3\rightarrow2} = 47.6 \pm 1.9$ kJ mol⁻¹ and $E_{2\rightarrow3} = 70.6 \pm 8.1$ kJ mol⁻¹, respectively. These results indicate that the closed-shell singlet structure is more inclined to transform to the open-shell triplet structure during the warming process.



Fig. 3 | **Bias-voltage-dependent measurements and regulation of the electronic structure via EEFs. a**, *I*-*t* curves (top), corresponding enlarged *I*-*t* curves (grey), and histograms (bottom) of the device connected with **NTCPhN** at different bias voltages. Conductance states 1, 2 and 3 are designated as red, blue, and yellow, respectively. **b**, Theoretically calculated EEF effects on the structural transition between the closed-shell singlet state and the open-shell triplet state. **c**, Voltage-dependent thermodynamic parameters of open-shell triplet and closed-shell singlet structural transitions and the variation of the average

lifetime of the open-shell triplet state with bias voltage at 300 K. **d**, Gibbs free energies of activation for the transition from the open-shell singlet and triplet states to the closed-shell state at different bias voltages. $\Delta G_{1\rightarrow2}^{\dagger}$ and $\Delta G_{3\rightarrow2}^{\dagger}$ represent the Gibbs free energy of activation for the conversion of conductance states 1 and 3 to conductance state 2, respectively. The error bars indicate the 1 σ confidence interval of a single-exponential fitting or errors propagated through the Eyring equation.

At the same time, variable-temperature experiments (Supplementary Figs. 24–26) conducted under other bias voltages demonstrate the effect of temperature on the transition between the singlet and triplet electronic structures transitions of **NTCPhN**. Notably, we find the effect of the electric field on the evolution of these electronic structures, which has rarely been reported in previous works.

Bias-voltage dependence

The well-defined, nanoscale gap of graphene electrodes ensures a sufficiently strong external electric field (EEF), which reorganizes the charge distribution of the molecule and stabilizes the resonance structure of the distribution, making otherwise difficult chemical reactions easier. Based on the approach used in the electric field catalysis^{39,48}, an electrostatic field was used to regulate the transition of singlet and triplet structures of **NTCPhN**. Figure 3a shows the *I*-*t* curves and the corresponding current distribution histograms of the device at 300 K with bias voltages of 0.05, 0.1, 0.2 and 0.3 V. As the bias voltage increased, the proportion of the high conductance state decreased and that of the low conductance state still dominated.

The relationship between ΔG and the electric field was obtained through theoretical calculation (Fig. 3b and Supplementary Table 2). Under the action of a stronger electric field, $|\Delta G|$ decreased linearly with an increase in the EEF. According to $\Delta G = -RT \ln K$ (where *K* is the equilibrium constant), ΔG was calculated at different voltages and linearly fitted (Fig. 3c). For convenience of analysis, we define $\Delta G = m \times V + \Delta G_0$, where *m* is the slope, *V* is the EEF strength and ΔG_0 is the ΔG value when there is no electric field. As there is a positive correlation between the EEF strength and bias voltage, *V* is replaced by *V*_d, and $m = -22.1 \pm 3.9$ kJ mol⁻¹ V⁻¹ is calculated, indicating that the electric field enhancement can reduce the potential energy difference between the two states and promote the transition from the closed-shell singlet state to the open-shell triplet state. The average lifetime of the low conductance state (τ_1) increased from 0.62 ± 0.08 ms to 4.53 ± 0.15 ms as the bias voltage increased (Fig. 3c and Supplementary Fig. 27).

Moreover, the Gibbs free energy of activation (ΔG^{\ddagger}) of the transition between each conductance state under different bias voltages can be calculated using the Eyring equation. As shown in Fig. 3d, $\Delta G^{\ddagger}_{1\rightarrow 2}$ increased whereas $\Delta G^{\ddagger}_{3\rightarrow 2}$ decreased with increasing bias voltage, indirectly indicating that increasing the bias voltage is favourable for the conversion of the closed-shell singlet to the open-shell triplet state. The effects of electric fields or temperatures on spin transitions have also been observed in other SMJs connected with **NTCPhN** (Supplementary Figs. 28–30). However, no such conductance state switching, indicative of spin state transitions, has been detected on electrical measurements of SMJs connected with **NTTPhN** or incompletely cut graphene ribbon (Supplementary Figs. 31–36).

Magnetic field dependence

Owing to the intrinsic spin properties of free radicals, which are sensitive to magnetic fields, spin states can be regulated by magnetic fields, as in the SQUID measurements. Referring to the reported work^{20,21}, we conducted the MR measurement of devices connected with **NTCPhN** at 4 K with a bias voltage of 0.03 V (Fig. 4a and Supplementary Fig. 37). All devices exhibited a positive MR with variations in the magnitude, which may be related to the strength of the molecule–electrode coupling and the spin polarization at the interfaces. In contrast, the resistance variation was found to be less than 8% at 300 K, probably



Fig. 4 | **Magnetic-field-dependent measurements and regulation of the electronic structures. a**, MR measurements on different devices of **NTCPhN**, **NTTPhN**, and incompletely cut graphene ribbon with a V_d of 0.03 V. MR is defined as $[R(B) - R(0)] \times 100/R(0)$ (%), where R(B) and R(0) are the resistances at magnetic field *B* and zero field, respectively. Blue curves represent the sweeping direction from -4T to 4T, and yellow curves represent the sweeping direction from 4 T to -4 T. **b**, *I*-*t* curves of the device (connected with **NTCPhN**) with magnetic field scanning at 4 K (a sweeping rate of 200 Oe s⁻¹ and a V_d of 0.1 V). The blue curve represents the sweeping direction from -6 T to 6 T, and the yellow curve represents the sweeping direction from 6 T to -6 T. **c**, *I*-*t*

curves, corresponding enlarged *I*-*t* curves (grey), and histograms of the device connected with **NTCPhN** at different magnetic fields, at a temperature of 300 K and a V_d of 0.3 V. Conductance states 1, 2 and 3 are designated as red, blue and yellow, respectively. **d**-**f**, Gibbs free energies of activation for the conversions from open-shell triplet to closed-shell singlet states (**d**), from closed-shell singlet to open-shell triplet and open-shell singlet states (**e**) and from open-shell singlet to closed-shell singlet states (**f**) at different magnetic fields. The error bars indicate the 1 σ confidence interval of a single-exponential fitting or errors propagated through the Eyring equation.

from noise-induced current fluctuations (Supplementary Fig. 38a). To further elucidate the MR properties originating from **NTCPhN**, we also performed MR measurements on the device connected with **NTTPhN** and incompletely cut graphene ribbon at 4 K, and the resistance of both varied less than 5% (Supplementary Fig. 38b,c).

Furthermore, during MR measurements, we observed a high conductance state in the low magnetic field range with a bias voltage of 0.1 V (a relatively large bias voltage for MR measurements), as shown in Fig. 4b and Supplementary Fig. 39. As the magnetic field decreased, the high conductance state gradually emerged, while it vanished as the magnetic field increased. Figure 4c shows the *I*-*t* signals and histograms under different magnetic fields. It is observed that the magnetic field has a subtle adjustment effect on the transition of the conductance state states. We obtained the average lifetime of each conductance state

(Supplementary Fig. 40) and further derived ΔG^{\ddagger} of the transition between each conductance state under different magnetic fields, as shown in Fig. 4d–f. As the magnetic field increased, $\Delta G_{11}^{\ddagger}, \Delta G_{21}^{\ddagger}$ and ΔG_{33}^{\ddagger} had decreasing trends, with ΔG_{21}^{\ddagger} decreasing the most, whereas ΔG_{23}^{\ddagger} had an increasing trend. These results, consistent with magnetic-field-dependent measurements at 0.1 V (Supplementary Fig. 41), imply that strengthening the magnetic field promotes the transition of the closed-shell singlet state to the open-shell triplet state and hinders the transition of the closed-shell singlet state to the open-shell singlet state.

It was calculated from the Gaussian peak area corresponding to each conductance state that the proportion of the intermediate conductance state remained at approximately 96%. To visualize the effect of the magnetic field on the singlet and triplet states, four periods of *I-t* data with a duration of 60 s under different magnetic fields were randomly selected for analysis (Fig. 4c and Supplementary Figs. 42–44). We counted the number of transition events of each conductance state under the different magnetic fields to reduce the statistical error generated by the low proportions of high and low conductance states, as shown in Supplementary Fig. 45. With the enhancement of the magnetic field, the number of events representing the low conductance state increased from 68 ± 4 (B = 0 T) to 305 ± 10 (B = 8 T), the intermediate conductance state increased from 97 ± 3 to 375 ± 6 , and that of the high conductance state increased from 28 ± 5 to 69 ± 5 . Obviously, the magnetic field has different effects on the transition of the molecule from closed-shell to open-shell singlet ground states as well as the triplet state, and the enhancement of the magnetic field facilitates the transition to the triplet state.

Conclusions

In summary, we integrated an individual diradical molecule into a single-molecule device platform and realized the direct detection and regulation of the spin states. The conversion from closed-shell to open-shell electronic structures was efficiently regulated using temperature, bias voltage, and external magnetic field. In addition, the corresponding thermodynamic and kinetic laws were elucidated. In particular, it was demonstrated that strong electric and magnetic fields facilitated the stabilization of the open-shell species and simplifies the complex structural analysis required for macroscopic detection. With further efforts to stabilize the quantum spin states at room temperature, this technique should provide important CMOS-compatible technical supports for the development of useful molecular spin-based quantum information systems.

Online content

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Methods

Molecular synthesis and characterization

All materials were commercially available and used as received. Commercially available reagents and chemicals were purchased from Energy Chemical and used without further purification. The synthetic route and characterization of the products are detailed in Supplementary Figs. 1–15.

¹**H-NMR and** ¹³**C-NMR.** The NMR spectra of the compounds were measured on a Bruker AV 400 MHz spectrometer in CDCl₃. Solutions tested in ¹³C-NMR were saturated. The high-resolution matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra of the sample molecules were obtained using a Bruker Agilent1290/maXis impact spectrometer.

Variable-temperature ESR spectra. The variable-temperature ESR spectra of powder samples were measured on a Bruker A300–10/12 spectrometer with a frequency of 9.651243 GHz. The experimental temperature covered the range of 100–300 K, and the molar amount of the sample was 0.02 mmol in a quartz ESR standard quality tube with an outer diameter of 4 mm.

SQUID. The magnetic measurements were carried out on a Quantum Design MPMS XL SQUID. The powder samples were sealed in a plastic capsule and measured in the temperature range of 100–325 K with an applied field of 5,000 Oe. The magnetic susceptibility of the samples

was fitted with the Bleaney–Bowers equation $\chi = \frac{2Ng^2\beta^2}{kT} [\frac{1}{3+e^{-\frac{N}{kT}}}]$, where

 χ is the magnetic susceptibility, *N* is Avogadro's number, β is the Bohr magneton, *g* is the magnetic field splitting factor, *k* is Boltzmann's constant, *T* is the temperature and *J* is the exchange integral after correction for the diamagnetic signal of the plastic capsule and sample holder, diamagnetism of the monomer, and paramagnetic contamination.

Device fabrication and molecular connection

Following a reported device preparation method^{40,41}, single-layer graphene was grown on the copper foil through chemical vapour deposition, divided, and transferred to a 0.8 cm × 0.8 cm silicon wafer substrate. Graphene ribbon with a width of 40 µm was then obtained through photolithography and oxygen plasma etching. Subsequently, photolithography and thermal evaporation were used to deposit arrayed metal electrodes (Cr/Au, 8/60 nm) to obtain graphene field-effect transistors (FETs). Then the windows were opened on the coated poly(methyl methacrylate) layer of graphene FETs adopting dashed-line electron-beam lithography. Finally, nanogapped graphene electrodes were prepared by oxygen plasma etching and electroburning. The fabrication of single-molecule FETs with a back-gate electrode necessitates the prior deposition of Al electrodes (40 nm) on a pristine Si/SiO₂ substrate. In addition, a 5 nm layer of HfO₂ is deposited using atomic layer deposition. The naturally oxidized Al₂O₃ layer and HfO₂ collectively serve as the dielectric layer, and the subsequent steps in the fabrication process remain as previously described.

We immersed the newly cut graphene device into pyridine with a molecular concentration of 10^{-4} mol l⁻¹ and added 10–15 equivalents (molar ratio) of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride to react for 2 days in an Ar atmosphere. After the reaction, the device was carefully cleaned with solvent and dried under a gentle N₂ flow, then placed into a metal box that shielded the device from static electricity. According to the *I*–*V* curves, the successful connection of molecules can be judged when the circuit changes from open to conducting state. Under optimal conditions, the success rate of molecular connection is approximately 18%, with 16 out of 89 electrode pairs demonstrating a conduction state in *I*–*V* measurements.

The probability of only one molecule contributing to charge transport is about 90% based on a binomial distribution analysis (Supplementary Note 1).

Electrical characterization

The *I*–*V* curves were measured using a Keysight B1500A semiconductor parameter system and a Karl Suss (PM5) manual probe station in an ambient atmosphere. *I*–*t* measurements were made with an UHFLIlock-in amplifier (Zurich Instruments Ltd.) and a DL 1211 current amplifier with a vacuum cryogenic probe station (Lake-shore TTPX) or physical property measurement system (Quantum Design). The current signals were recorded using an acquisition card from NIDAQ at a rate of 54,930 samples s⁻¹.

Theoretical calculation

We have performed computational calculation to get insight into the molecular geometry, geometric parameters and aromaticity of the molecule (Supplementary Note 2 and Supplementary Figs. 46–49), referring to a previous work²⁸. The singlet and triplet states of **NTCPhN** are fully optimized without any imaginary frequency in Gaussian16⁴⁹ using hybrid density functional B3LYP with 6–31 G(d,p) basis. The diradical (y_0) and tetraradical (y_1) character are assessed using the spin-projected unrestricted Hartree–Fock method with Yamaguchi's formula⁵⁰ at UHF/6-311G(d) level of theory and basis set. Nucleus-independent chemical shift (NICS_{iso}(1)) is computed with gauge-independent atomic orbital method⁵¹ at 1 Å above the rings plane. Finite-temperature density functional theory calculations are preformed using ORCA program package⁵². The fractional occupation number weighted electron density (N_{FOD}) is computed by the reported method⁵³, and molecules with a large N_{FOD} will have a multireference character⁵⁴.

The transport simulations of single-molecule device are performed using density functional theory combined with the nonequilibrium Green's functions^{55,56}, as implemented in Atomistix Toolkit software (version R-2022.12)^{57,58}. The transport device model is divided into three parts, that is, left electrode, central region and right electrode. Both electrodes are semi-infinite p-type doped graphene. For the optimization of device structures (Supplementary Figs. 50 and 51), the criterion for the total force and energy are set as 0.05 eV $Å^{-1}$ and 10^{-4} eV. A k-point mesh of $4 \times 1 \times 150$ and 3×1 is utilized for device self-consistent calculations and transmission spectra calculations, respectively. The generalized gradient approximation with spin-dependent Perdew-Burke-Ernzerhof functional is employed to describe the exchange-correlation potential⁵⁹. Furthermore, a further confirmation is conducted on the transmission spectra of Perdew-Burke-Ernzerhof functional by utilizing Heyd-Scuseria-Ernzerhof hybrid functional method⁶⁰, revealing their qualitative consistency in the results.

Statistics and reproducibility

No statistical method was used to pre-determine sample size. No data were excluded from the analyses. All relevant information is stated in the figure captions or Methods. Data are presented as mean \pm standard deviation. The errors arise from the average lifetimes fitted by the single-exponential model and the subsequent data propagated through formula calculations, including ln*k*, *E*_a and ΔG^{\ddagger} . The results of temperature-, bias voltage- and magnetic field-dependent experiments have been reproduced in three or more devices.

Data availability

The data supporting the findings of this study are available within the paper and Supplementary Information. The datasets used in Supplementary Information are available online from the Zenodo repository at https://zenodo.org/records/10603012. Source data are provided with this paper.

Article

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Author contributions

X.G., F.H. and Y.L. conceived the idea for the paper. C.Ya., J.C. and G.K. fabricated the devices and performed the device measurements. Z.C., W.Z., W.L., J.H. and W.C. carried out the molecular synthesis and characterization. C.S., M.A.S. and N.R. performed calculations for the analysis of the open-shell character and aromaticity. C.Yu., X.L. and J.Y. built and analysed the theoretical model and performed the quantum transport calculation. X.G., F.H., Y.L. and C.Ya. analysed the data and wrote the paper. All the authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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