nature portfolio

Peer Review File

Unraveling the dynamics of multiple excited states in a single-molecule transistor

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Parts of this Peer Review File have been redacted as indicated to remove third-party material.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
General Comments
The authors present an interesting study on the excited-state dynamics of an open-shell single-molecule radical using a nanosecond pump–probe technique. The observation of multiple excited states and their continuous energy relaxation is a significant contribution to the field of single-molecule electronics. The work effectively combines transport measurements with TDDFT calculations to construct a comprehensive picture of the interplay between charge and spin states. Overall, the manuscript is clearly written and the experiments appear carefully designed. I support publication of this work; however, there are a few aspects regarding the physical interpretation and data presentation that, in my opinion, would benefit from further clarification.
Specific Comments
1. Clarification regarding the mechanism of the energy shift
The manuscript attributes the continuous energy shifts observed in Peaks 2 and 3 (Fig. 4b) to interaction energy re-normalization associated with transient fractional charge states during the relaxation process. This interpretation is intriguing, but I would appreciate some clarification regarding its scope. Typically, Coulomb renormalization resulting from a variation in the molecular charge state implies a modification of the global electrostatic potential. Such a change should, in principle, affect the energetic barrier for all tunneling events, including the ground state. However, the data in Fig. 4a and 4b show that Peak 1 (attributed to the ground state D0+) remains energetically stable throughout the delay time, in contrast to the significant shifts seen in Peaks 2 and 3.
Could the authors elaborate on why the ground-state signal appears not to be significantly affected by this potential change? A brief discussion of whether this behavior points towards a state-specific relaxation mechanism rather than a global Coulombic effect would be helpful. In addition, regarding the “transient fractional charge states”, it might be worth commenting on whether the static DFT/TDDFT models employed are sufficient to capture the energetics of a dynamic system where rapid electron exchange with the electrodes may be involved.
2. Transport data
The charge stability diagram in Fig. 2b suggests that at VG = –2.5 V, the conductance onset occurs around VSD =±0.2 V. However, in the pulsed spectrum shown in Fig. 2c, the signal in this voltage range appears less distinct compared to the excited-state resonance at –0.7 V. I understand that pulsed measurements have different noise characteristics, but could the authors comment on the visibility of the ground-state transport channel in the pulsed setup?
3. Technical details and presentation
(1) Fig. 2d inset: In the schematic illustrating the pump excitation process, both the lower and upper energy levels are labeled as D0+. Since the pump pulse excites the molecule to a different charge state, labeling the excited level as the ground state D0+ is confusing and appears to be a typo.
(2) Energy scale in Fig. 3b: It would be helpful to state explicitly whether the y-axis (“E”) represents the absolute energy relative to vacuum, or energy relative to the Fermi level.
(3) Citations/cross-references: There appears to be a cross-referencing inconsistency where the text mentions “section S7”, while the Supplementary Information currently contains sections only up to Section IV. Please check and correct the section numbering.

Reviewer #2

(Remarks to the Author)
Zhang et al. developed an electronic pump-probe method to access different electronic states of a single-molecule transistor, similar to pump-probe methods used in scanning probe microscopy. Using a pump-probe scheme, they observe three clear signals, of which two have a time-dependency on a timescale of a few 100 ns, indicating transitions into different electronic states.

As an expert in scanning probe microscopy, I do not see that the work adds new insights to the understanding of excited-state dynamics. The authors correctly cite the relevant scanning probe microscopy works, in which excited-state energies and lifetimes can be accessed. Incorrectly the authors state that 'the excited state dynamics of open-shell radical remains inaccessible due to the lack of appropriate external gate in STM configuration'. Yes, there is a lack of external gate in STM, but nevertheless open-shell radicals can be studied, as in reference 39. In addition, in AFM on thick insulating films, a gate voltage is applied, allowing the access to different open-shell configurations, see e.g. reference 22. Indeed, in a single-molecule transistor you can apply a gate and source-drain voltage, which might have advantages over scanning-probe microscopy, but these advantages are not apparent from the current work. I do therefore believe that this work is not suitable for Nature
Communications.

My main criticism of the current work is in the interpretation of their data. The authors make various claims, of which some seem incorrect and others are not properly supported:
• Line 166 'The long lifetime also supports the involvement of spin flipped state, i.e. triplet state'. Indeed, spin-forbidden transitions have a long lifetime. However, it seems from this paper that the authors are probing charge transitions and not the transition from the excited triplet state into the ground singlet state. In that case, the different time scales could be explained by different tunneling rates and are not dependent on the lifetime of the excited state, but on the lifetime of the charged states.
• The authors assign the observed peak in Fig. 3 to the S02+ and T12+ states. They are close in energy, so it could be that they are indeed both accessed. The authors do not explain well why they assign the peak drop to accessing the T12+ state (I would have naively assumed the peak itself is then due to accessing both S02+ and T12+). In other words, why is the S02+ a low-conductance state and the T12+ a high conductance state, as the authors write?
• It is not clearly explained how, by increasing the pump voltage, first a transition into S0 and later a transition into S02+ and T12+ is opened in Fig. 3b. It would be helpful to make the connection between Fig. 3b and the applied pump voltage. Is the pump voltage (times a lever arm) reflected in the length of the arrows? Are the levels itself also shifting when the pump voltage is changed because of the lever arm?
I am also very surprised that the transition from D0+ into S0 doesn't show a clear resonance, but the one into S02+ and T12+ does, maybe because the transition to S0 is opened all the time? In addition, it seems that the signal being measured is a time-average over a single molecule, which could explain the increase in tau with pump voltage by changing the ratio of tunneling into S0 vs S02+/T12+ which seem to have a lower tunneling rate to decay back to D0+.
• Line 210-212: 'In contrast to the single-pulse differential conductance spectra, two new resonant peaks (Peaks 2 & 3) appear in the positive probe voltage regime, indicating they are transient species generated by excited states after the pump pulse.' Do the authors here refer to Fig. 2c? There is a clear shoulder at 0.5 to 1.0 V, which indicates that these signals are already present there. The authors also see them at 0 delay time in Fig. 4a. Thus, it is not clear to me why they are only generated after the pump pulse, as the authors claim.
• I got very confused by comparing Fig. 2e (please mention there in the caption the used probe voltage) and Fig. 2f, especially since Fig. 2e only shows negative pump voltage and not positive ones. The authors do not properly explain the different effects of the pump and probe pulse, making it challenging to interpret these two plots. I think it would have been very helpful to explain first in more detail what only the pump pulse does. Is there for instance a dependence on the pulse width of the pump pulse?
• Line 217/218: Why do T12+ and S02+ transfer to a Dn+ state and not directly to D0+? If the molecule is in T12+, you can tunnel an electron in the lower level and for S02+ into the first empty level.
• One of the main claims of the paper is that the energy of the T12+ and S02+ states are changing with the pump-probe delay time. The authors do not support enough evidence for this claim. They write (line 222) 'While there is one possibility the electronic pump-probe technique could theoretically average discrete quantum transition events into smoothed Iprobe-Vprobe responses through repetitive excitation cycles, the observed 220 meV energy resolution (evident in the energy difference between Peak 2 and Peak 3 at t = 0 ns) contradicts this interpretation, as the 440 meV shift of Peak 2 substantially exceeds this resolution limit.' The fact that the energy resolution between the two peaks is 220 meV, doesn't mean that the two peaks cannot represent an average population. Only that the two peaks seem to reflect two independent pathways. I believe that the first part of their sentence is actually giving the right interpretation. They also illustrate this in Fig. 4b, they transfer from T12+ into D0+ and S02+ into D0+. So what if the peak energy they measure is reflecting the average between T12+/S02+ and D0+, and is shifting in energy because of the changing populations?
• The authors also claim 'provides direct evidence for meta-stable molecular states with fractional charge occupancy'. I do not see this claim to be justified. It seems the molecule is either 2+ or +, but a time averaged is e.g. showing 1.5+.
• Line 263/264: 'The strong electric field interacting with dipole moments results in the energy splitting observed in relaxation process of S02+ and T12+'. The authors did not elude to this before. They even excluded the effect of the electric field. It seems that this statement in the conclusion is thus not well-supported by the claims made in the results.

Some minor criticism:
• It is not clear if the authors use the word excited state for any state that is not the ground state, e.g. also ground states of other charge states, or only of excited states of a particular charge state.

• The pulse width experiment performed for single pentacene molecules is quite different from the one presented here. The similarity is that a pulse length is swept, but there are many examples of such experiments in literature. I would omit the reference to Jinbo et al. in line 112.
• Line 159/160, reference 39 is about a different molecule. So this sentence should be omitted or rephrased.
• The authors write in line 164 that D1+ has a lifetime of 4.7 ns. How do they know?
• SI page 11 Fig. S13, in the caption it is written Vg = 0 V for b, but in panel b it is written Vg = -2.5 V. In the same figure, why didn't the authors take the same time region to determine the slope in a and b?

Reviewer #3

(Remarks to the Author)
The paper presents a nanosecond pump-probe study of the excited state dynamics of a single molecule measured by placing the molecule in a transistor device. The main claim of the paper is that this type of experiment allows the authors to access the excited state dynamics of open-shell radicals, which goes beyond what STM-based techniques can achieve. I deem the results to be of high quality and broad interest to the community of researchers studying excited state dynamics at the single molecule level. However, the presentation of the paper needs improving, before it is suitable for publication in Nature Communications. Here is a list of specific points I would like to see addressed by the authors, as well as a few general comments on the presentation.
1. The introduction needs to be expanded on to make it clear why these results are interesting to a broader audience. Moreover, the introduction is a bit confusing as it leaves the reader with the impression that this is an STM study of a device. It is not clear why open shell radicals are inaccessible with STM techniques and how this study goes beyond that.
2. Figure 1 caption needs to explain everything that is in the figure.
3. It is not clear how it was established that the transistor contains a single molecule. Can you give a concise argument within the main text?
4. Line 110 states that the experiment was repeated with another molecule. Can you be more precise about what molecule was used and how it differs from the original molecule? How does this support the claims of the paper?
5. Were the spectra in Fig 2 reproducible? Did you repeat the measurements showing the emergence of -0.8 V state?
6. Fig. 3c &d need more explanations in the caption.
7. Is the pump-probe data you acquired sensitive to the molecular orientation in the device? Did you perform measurements on more than one molecular device?
8. The claim on line 246 that this is the first experimental observation of multiple excited state relaxation dynamics needs checking, cf Ferreira, et al Nat Commun, 16, 6039 (2025).
9. Please fix grammar and spelling mistakes across the paper.

Overall, I recommend the paper for publication, subject to answering the issues I raise above and improving the presentation.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed all my concerns with new data and refined interpretations; therefore, I recommend the work for publication in Nature Communications.

I have carefully re-read the revised manuscript, the detailed comments from Reviewer 2, and the authors' point-by-point responses. My overall view remains that the experimental work is interesting and that the observation of pump-induced transient spectral features in a gated single-molecule junction is potentially valuable. The revised manuscript has also addressed several of my previous methodological comments.
However, after examining Reviewer 2's criticisms in detail, I think that Reviewer 2 is definitely an expert in the field and several core physical questions raised by him/her are indeed substantial and, in my opinion, have not yet been fully resolved by the revised revision. My main concern is not necessarily the experimental observation itself, but rather the strength and specificity of the microscopic interpretations currently attached to it. I believe the manuscript would benefit from a more cautious distinction between what is directly established by the experiment and what remains a plausible, but not uniquely demonstrated, microscopic assignment.
1. The discrepancy between expected charge-transfer rates and extracted lifetimes
I agree with Reviewer #2 that the current interpretation tends to associate the observed hundreds-of-nanoseconds delay dependence directly with the intrinsic lifetime/evolution of specific doubly oxidized states. There appears to be a quantitative discrepancy here that needs to be addressed. In Reply 2-4, the authors argue for sufficiently strong molecule–electrode coupling in the source–drain junction and, on that basis, for an effective bias lever arm close to unity. At the same time, the measured steady-state currents can reach the nA range (Figs. S6 & S7). In such a scenario, it is difficult to reconcile the extremely long apparent lifetimes (hundreds of nanoseconds) assigned to the dication (N–2) states with the expected ultrafast (e.g., picosecond) charge-transfer rates of the junction. It remains plausible that the measured time dependence reflects a more composite nonequilibrium recovery process—such as slower electrostatic/conformational relaxation of the junction environment—rather than the intrinsic lifetime of the proposed (N–2) molecular states. A more quantitative

discussion would be helpful. Even a minimal rate-equation or master-equation picture, with reasonable bounds for charge-transfer and relaxation pathways, would substantially strengthen the interpretation and help clarify whether the measured time constants can be consistently associated with the proposed charged states.
2. The assignment of Peaks 2 and 3 remains largely qualitative
I also find Reviewer #2's concerns on the microscopic state assignment well taken. The interpretation of the transient features still relies heavily on qualitative gas-phase TDDFT level schemes and on an assumed correlation between probe bias and specific many-body transitions.
While the proposed picture is certainly suggestive, correlating gas-phase computational energy levels directly to experimental transport resonance voltages is inherently complex and typically subject to significant environmental shifts within the junction. In its current form, the TDDFT calculations provide a qualitative schematic rather than a rigorous quantitative proof of the specific many-body assignments. The evidence therefore appears more consistent with the proposed pathway than uniquely proving it. I would encourage the authors to soften the wording accordingly and avoid overstating the microscopic specificity of the proposed transitions.
3. Alternative explanations for the delay-dependent peak motion
Reviewer #2's concern regarding the delay-dependent peak shift is also substantial. The revised manuscript discusses global/differential shifts and dipole effects. However, it remains unclear to what extent the observed continuous peak motion can be uniquely attributed to genuine state-energy evolution of the molecule, rather than to population averaging, time-dependent competition between multiple channels, or slower electrostatic/environmental reorganization of the junction. Since these alternative explanations have not been convincingly excluded, I suggest that this part of the interpretation be presented in a more restrained way, making it clear that the proposed mechanism is a plausible interpretation rather than a uniquely established conclusion.
4. Clarification of Fig. 3b
As a smaller but still relevant point, the meaning of the energy axis in Fig. 3b may benefit from further clarification. The authors state in the rebuttal that the axis refers to "the absolute energy relative to the vacuum level". If so, the figure could be easily misread as showing absolute energetic separations (e.g., total energy differences or ionization potentials) between different charge states, which typically reside on a different energy scale. It would be helpful to state more explicitly whether Fig. 3b is intended as a quantitative total-energy diagram or as a schematic relative-state alignment.

Reviewer #2

(Remarks to the Author)
I want to thank the authors for the effort they put into trying to improve the manuscript. This helped me to further grasp the results and interpretation of the authors. Fig. 2f shows now a spectrum which is similar to the ones obtained in Nat. Nanotechnol. 2025, 20, 27, but in this case with a limited number of signals and less variation in the pulse schemes, and without the ability to assign the peaks based on essentially only the measured spectra (no DFT is necessary in Nat. Nanotechnol. 2025, 20, 27). The further analysis of the experimental data as presented in Fig. 3 and 4 is largely a misinterpretation of the signals, leading to the false claims about states that strongly shift in energy. In addition, the single-molecule junctions are poor to reproduce, which makes it very challenging to derive any quantitative information from these measurements. I, therefore, strongly suggest rejecting this paper.

Please find below an elaborate discussion of the incorrect statements.
1. The authors compare their data with data presented in Phys. Rev. Lett. 2021, 126, 176801 (Fig. R3). They wrongly state in their rebuttal that in the cited paper the measured data points correspond to the lifetime. Instead, they are the probability that a single electron tunneled during a certain time interval, in other words, they represent a tunneling current. That is why the authors of that paper took a derivative to obtain the energies of the involved states. The authors of the paper under review measure similar curves as presented in Fig. 2f. If they want to reproduce the results from Phys. Rev. Lett., they should then take the derivative of that data, not of the extracted decay rates of the various features observed. In addition, the authors compare their data with Nat. Nanotechnol. 2025, 20, 27 (Fig. R2). Again, they should compare Fig. 2f with this data, and then the authors see that there curves also do not shift in voltage with increasing times, but simply reduce in magnitude. The authors should therefore:
a. Remove the statement: 'Interestingly, the non-quantized correlation between lifetime and pump voltage around Vpump = -0.8 V is distinct from the quantized excited state dynamics in an individual naphthalocyanine molecule where the lifetime against the voltage exhibits the plateau-like feature39. Such a discrepancy suggests the appearance of coherent transition between multiple excited states.'
b. Remove the dtau/dV curve from Fig. 3a.
c. 'The shift in the branching ratio of transitions into S0 and S02+/ T12+ leads to the observed increase in with pump voltage.' I believe that the observed increase in decay time is because the population of both S02+ and T12+ are increasing.
d. 'This closer proximity implies a higher tunneling probability for T1, which accounts for Gaussian-shaped Iprobe regime around Vpump = 0.8 V in Fig. 2f.'
i. The authors do not explain why at negative and positive gate voltages S02+/T12+ are accessed? In AFM experiments at negative and positive gate voltages different charge states will be accessed. It would be helpful if the authors draw the full many body diagram at different gate voltages to explain this, as well as illustrate this in single-particle pictures. The fact that it is accessed at both positive and negative gate voltages could be explained by the drain and the source being present. However, this is in contrast to figure 4d, where it is indicated that at positive gate voltages S02+/T12+ are emptied, not occupied.
ii. In addition, the Gaussian-shapes are explained in STM/AFM experiments by the phonon-induced broadening because of the underlying NaCl surface. In the manuscript under review the signals at positive and negative gate voltage are similarly broadened, the authors should explain what the origin of this broadening is.

iii. The reduction of the signal at -1 V in 2f and 3a could be explained by opening an additional decay channel at higher applied gate voltages. The authors do not consider such decay pathways during the applied probe pulse.
2. Related to Fig. 4a:
a. The negative signal is nicely explained by re-excitation of D0+ to doubly charged states. Because of the broadening of the peak, I would explain the fact that the signal appears earlier at -1 V then at -0.7 V by the fact that the tunneling rate is faster at higher applied voltages. This is also in line with the abovementioned potential faster decay of S02+ and T12+ at -1 V. It is also hard from plot b to see the signal between 0 and 100 ns delay time.
b. In case of peak 2 and 3: I would explain the shift of the signal in that case to a difference in tunneling rate if you are well above the resonance peak or if you are at a tail, where the tunneling rate is lower. In other words, at short delay times you can only tunnel well above the resonance peak, while you need longer delay times to also be able to tunnel at the tail.
c. This is related to the presentation in Fig. 1: Probe phase seems to imply that the energies of S02+ and T12+ reduce till they are at the level of D0+, however, I believe the energies stay the same, but the way the signal is being probed it appears to be a shift.
3. The authors already indicate that: 'The fine feature of pump-probe data is highly sensitive to the molecular orientation and gap size which affects the charge transfer rates, resulting in the incomparability of different devices'. They also state in the caption of Fig. S12 that the 'dynamic behavior of Device 2 shown in Fig. S12b was 221 essentially consistent with the phenomena previously observed'. They hardly show any data for Device 2, which makes it hard to compare. The limited data already hints at a slightly different lifetime. In other words, the authors need to tone down drastically their claims about lifetimes, they measure always decay times which are highly sensitive to the exact fabrication of their device.

Other comments:
4. Fig. 2c: Is Vpulse the same as Vpump later on? The authors describe their pump-probe pulse sequence and then it is confusing that they suddenly introduce a pulse in general. In my understanding that is the same as Vpump, and the authors should rename it.
5. In Fig. 2e, the authors show data for a pump pulse with a delay time, there is no probe pulse mentioned, what does the delay time then represent?
6. 'We attribute this difference to the negative bias exciting a discrete state (corresponding to the sharp peak at -0.65 V in Fig. 2c) with a low dephasing rate, whereas the positive bias excites a continuum state (corresponding to the broad shoulder at 0.5–1.0 V in Fig. 2c) exhibiting a much higher dephasing rate.'
Comparing Fig. 2c up and down panel it is not apparent at all that the peak is sharp at -0.65 V and continuum at 0.5-1.0 V. There is also a background signal at top panel. As far as I understand the authors could just omit the statements about discrete and continuum and only focus on the dephasing rates? If they want to make this point they should show clear data that these peaks are sharp versus continuum.
7. In the caption of figure 2: 'The inset illustrates that the D0+ can be set to a virtual state (dashed line) with high energy' The energy of D0+ is raised by the applied voltage, it is not a virtual state, please rephrase (the authors show this also correctly in another figure).
8. I assume Fig. 3a is derived from fitting the data in Fig. 2e, the authors should explain this better. Why do they only show the data for negative gate voltages and not also for positive gate voltages?
9. 'Since differential conductance is proportional to the density of state, the value of Gtransient presented in Fig. S22 could indicate the population of electrically stimulated transient species' That would mean that the density of states is the same for every of the states, and the tunneling barriers are the same. This can essentially be ruled out because there are different orbitals involved with different tunneling barriers and different coupling to the leads.
10. Related to Fig. S13: What is the relation between panel b and d? If the lifetime is extracted from the data in panel b, then it seems the lifetime/decay time is similar for the whole range of gate voltages between 0.5 V and 2.5 V. Fig. S13c is also not helpful at all to try to explain a difference in lifetime. If there is a real effect here, I believe it is again due to the broadening of the states.
11. In STM configurations you can also have molecules with an out-of-plane dipole, e.g. if the molecule is not flat. The authors should add the word typically in their new sentence:
However, the typically orthogonal alignment between electron transport direction and dipole moments of excited states renders the weak electric-dipole interaction.
12. The authors should check the English in the paper; there are many mistakes leading to many sentences that cannot be easily read.

Reviewer #3

(Remarks to the Author)
I am satisfied that the changes made by the authors resolved the issues that I raised previously and I recommend the paper for publication in Nature Communications.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I have carefully read the revised manuscript and the authors' responses to the referees. I agree with Reviewer #2 that the

precise microscopic assignments, including the origin of the apparent nanosecond energy drift and its relation to specific many-body states, remain somewhat interpretative and are not uniquely established by the current data.
However, I note that the authors have made reasonable efforts to soften their claims and present their interpretation in a more cautious manner. In my view, the main contribution of this work lies in the experimental methodology and the observation of non-equilibrium charge dynamics in a single-molecule device, which is novel and valuable.
Therefore, I maintain my recommendation that the manuscript can be accepted for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)
I thank the reviewers for answering my questions and concerns and clarifying and resolving most of them. In a few cases, I misunderstood the author's statements, and I want to thank them for clarifying them in their rebuttal. There is one remaining issue where we have not reached a consensus yet, after resolving that issue, I am fine if the manuscript is published.
My issue is related with Fig. 4, and its interpretation. I still cannot believe that the states are actually shifting in energy during the delay time, and the authors do not provide sufficient proof for these statements, and do not clearly exclude other effects. Already in accordance to the feedback of reviewer 1 the authors slightly toned down their statements, but the authors still clearly claim that the states shift in energy.
The authors write in their rebuttal: 'we respectfully disagree with the interpretation that "the signal appears earlier at –1 V than at –0.7 V due to a faster tunneling rate at higher applied voltages". As shown in previous work (Nat. Commun. 2023, 14, 4988), once the excitation energy exceeds the tunneling barrier, the tunneling rate (lifetime of charged state) no longer increases significantly with increasing bias. Therefore, the earlier appearance of the signal at –1 V cannot be attributed to a higher tunneling rate.' The authors incorrectly compare to this paper, where special measurement conditions are employed under saturation conditions. Under such saturation conditions the signal is independent of the bias voltage. The observation of non-step like features in Fig. 1f indicates that the authors do not work under these conditions, and therefore, they should compare with the results from Phys. Rev. Lett. 2021 and Nat. Nanotechnol. 2025, as they also did at other places in the manuscript. There it is clearly visible that the signal still increases till a plateau is reached. I believe that the results in Fig. 4a are similar as in those papers, and therefore that the results in Fig. 4b cannot be interpreted as a shift of the energies of the states.
The authors later on even acknowledge: 'While variations in tunneling rate, such as those arising from accessing the tail versus the center of a resonance, may in principle influence the signal', but then state that 'they are not expected to produce the systematic energy shift observed here.' The argumentation why that is not the case they provided earlier, and there I disagree with.
I strongly suggest removing this interpretation of a shift of the state energy in Fig. 4 and the corresponding description and instead propose several reasons for the observed data in Fig. 4b, including the statement they already have about the averaging, as well as a statement about the influence of the broadening of the peaks.
Minor feedback:
1. Related to Fig. S13: I thank the authors for their explanations and agreeing that the change in lifetime is related to the energy broadening of the state. I believe that the energy broadening causes the population of the state to change, and thereby the observed lifetime of the average occupied state. Could the authors add that to the caption, for instance like: The lifetime initially exhibits an upward trend (between –0.5 V to –2 V) because of the energy broadening of the involved state, 'increasing the population of the excited state with increasing voltage'. However, once the excitation energy provided by exceeds the energy broadening of the excited state, the 'population and therefore the' lifetime reaches a plateau and remains almost entirely unchanged (between –2.5 V to –4 V).
2. Related to Fig. 2e, it would be helpful if the authors explicitly listed the probe pulse parameters in the caption of Fig. 2e (e.g. Vprobe = -1 V), even though they are, as the authors rightfully pointed out, indeed already mentioned at other places.

Reviewer #3

(Remarks to the Author)
I have reviewed the extra comments made by reviewers 1 & 2 and the responses given by the authors. I believe that the quality and clarity of the manuscript have sufficiently improved as a result of the changes made by the authors. The authors' explanation is reasonable, though a minimal illustrative rate-equation sketch could still help address the recurring concern about timescales. I offer this only as a tentative suggestion and defer to the judgement of the other reviewers and the editor. I recommend the article for publication in Nature Communications.

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Point-by-point responses letter to reviewers' comments

Reviewer #1 (Remarks to the Author):

General Comments

The authors present an interesting study on the excited-state dynamics of an open-shell single-molecule radical using a nanosecond pump–probe technique. The observation of multiple excited states and their continuous energy relaxation is a significant contribution to the field of single-molecule electronics. The work effectively combines transport measurements with TDDFT calculations to construct a comprehensive picture of the interplay between charge and spin states. Overall, the manuscript is clearly written and the experiments appear carefully designed. I support publication of this work; however, there are a few aspects regarding the physical interpretation and data presentation that, in my opinion, would benefit from further clarification.

Specific Comments

1. Clarification regarding the mechanism of the energy shift

Comment 1-1: The manuscript attributes the continuous energy shifts observed in Peaks 2 and 3 (Fig. 4b) to interaction energy re-normalization associated with transient fractional charge states during the relaxation process. This interpretation is intriguing, but I would appreciate some clarification regarding its scope. Typically, Coulomb renormalization resulting from a variation in the molecular charge state implies a modification of the global electrostatic potential. Such a change should, in principle, affect the energetic barrier for all tunneling events, including the ground state. However, the data in Fig. 4a and 4b show that Peak 1 (attributed to the ground state D0+) remains energetically stable throughout the delay time, in contrast to the significant shifts observed in Peaks 2 and 3.

Could the authors elaborate on why the ground-state signal appears not to be significantly affected by this potential change? A brief discussion of whether this behavior points towards a state-specific relaxation mechanism rather than a global Coulombic effect would be helpful. In addition, regarding the "transient fractional charge states", it might be worth commenting on whether the static DFT/TDDFT models employed are sufficient to capture the energetics of a dynamic system where rapid electron exchange with the electrodes may be involved.

Reply 1-1: Thanks for your helpful comment.

(1) Regarding the fractional charge states we used here, they imply the total charge states of molecule and electrodes rather than the concept of fractional charged quasiparticle itself. Generally, the charge state of a single molecule is absolutely quantized which indicates a two-state fluctuation expected in continuous d.c. measurements from the communities of AFM and STM (***Science*** 2004, 305, 493; ***Nat. Nanotechnol.*** 2018, 13, 376). However, the continuously changing in dynamics indicates that the re-normalization happens at the single-molecule level, which couldn't be simply interpreted by quantized charge states of molecular junction.

(2) To describe the impact of Coulomb renormalization, we introduce the concept of fractional charge states contributed by both single molecule and electrodes to describe the system. We do see the energetically variation of Peak 1 at the early stage by rechecking the dataset. A new **Fig. 4** is presented, where we observed the shifts of Peak 1 and Peak 3 are synchronized (a modified **Fig. 4e** and a new figure of **Fig. S22**). Therefore, we attribute them to an energy level renormalization driven by the dissipation of total molecular charge, which is considered as global electrostatic potential

shift (***Nat. Nanotechnol.*** 2013, 8, 282). And there is a tiny change in the energy space between Peak 2 and Peak 3, which is considered as differential electrostatic potential shift. It indicates the initial energy space between Peak 2 and Peak 3 has been changed by the pump voltage due to the electric field coupling with dipole moment. This is the first observation of such a strong coupling effect in single-molecule scale. A previous example in STM studies only shows hundreds microelectronvolt shift driven by electric field (***Science*** 2021, 373, 95).

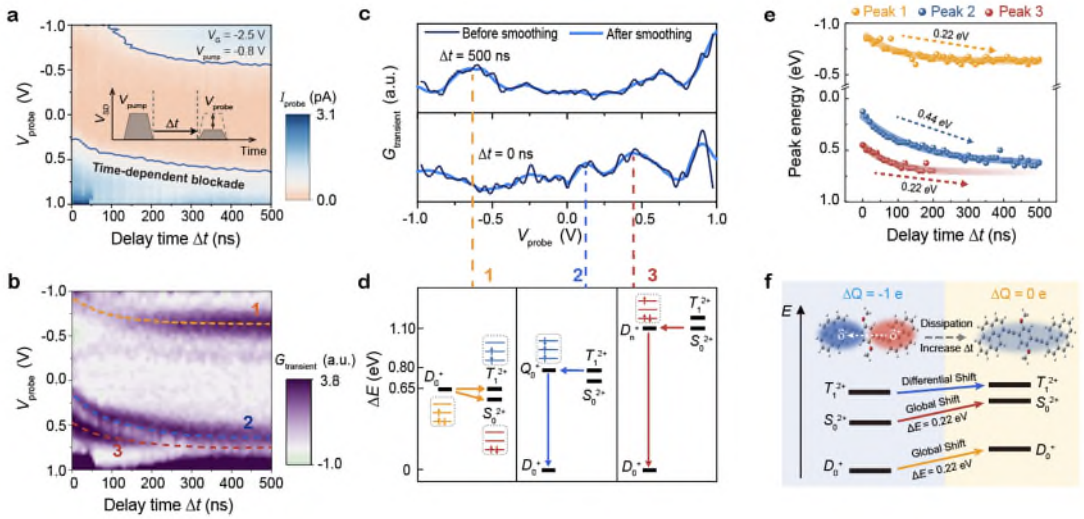


Fig. 4 Transition pathways and Coulomb interaction among excited states. (**a**) Corresponding dependence of the probe current I_{probe} on the delay time as a function of probe voltage V_{probe} after a fixed pump voltage V_{pump} = –0.8 V at a continuous V_G = –2.5 V. (b) Transient differential conductance spectroscopy derived from (**a**). Each differential conductance curve is smoothed with a Savitzky–Golay filter with a window length of 11 for better recognition. (**c**) Selected differential conductance derived from (**b**) before (black) and after (blue) smoothing at Δt = 0 ns (lower panel) and 500 ns (upper panel). (**d**) Schematic of transition pathways of peaks 1-3. Peak 1 appears at long delay times, where the population of the D_0^+ state is higher, and is therefore attributed to a re-excitation process involving transitions from D_0^+ to S_0^{2+}/ T_1^{2+}. Peak 2 originates from the contribution of the T_1^{2+} state and corresponds to the transition from T_1^{2+} to Q_0^+. Peak 3 corresponds to the transition from S_0^{2+} to the D_n^+ state. (**e**) Peak energy extracted from (**a**). The lines are guides to the eye. **(f)** Illustration of Coulomb interactions among excited states, including a global energy shift and a differential energy shift during charge dissipation.

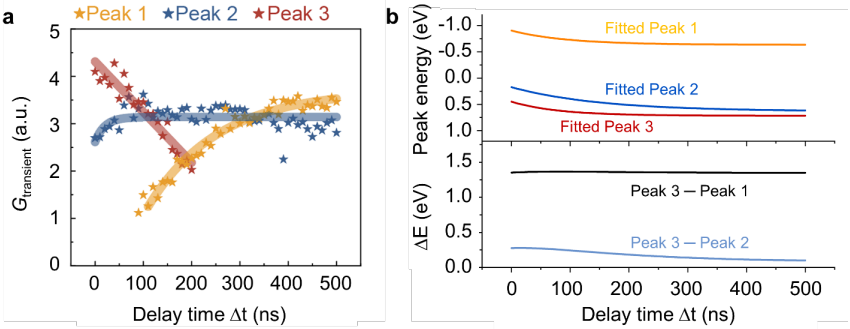


Fig. S22 The time evolution of peak intensity (a), energy (top panel of b) and energy space (bottom panel of b) among Peak 1, Peak 2 and Peak 3 shown in Fig. 4b.

We modified the related discussion in the main text (Page 9 Line 296-301 & Page 10 Line 313-324)

and as follow:

"We extract the peak energies of them at every delay time presented in **Fig. 4e**. The energy of D_0^+ (Peak 1) and S_0^{2+} (Peak 3) shift synchronously, suggesting the ground states of each redox states is dependent on the global energy shift by Coulomb renormalization[39]. Notably, the energy of S_0^{2+} and T_1^{2+} shifts distinctly with delay time, where the central energies of Peaks 2 and 3 exhibit a continuous downward shift of ~ 440 meV and ~220 meV within ~150 ns, respectively. "

"Thus, we can summarize the energy evolution in **Fig. 4f**. The overall energy shift is likely driven by renormalization dominated by charge dissipation, which is supported by the synchronous shift. Meanwhile, the evolution of the energy gap between S_0^{2+} and T_1^{2+} points to a state-specific relaxation: the initial 220 meV gap may be amplified by the rapid stabilization of the T_1^{2+} state relative to S_0^{2+} due to their differing dipole moments. This phenomenon is exclusively observed in single-molecule radical junctions where charge transport is parallel to the molecular backbone direction, enabling enhanced many-body coupling between transient charges and molecular orbitals. An example in STM study shows that the orthogonal coupling between electric field and molecular dipole only induces a microelectronvolt shift[50]. Our finding provides the direct measurement of multiple excited-state relaxation dynamics induced by electrical stimuli in single-molecule transistor."

(3) Regarding the mechanism of state-specific relaxation, we have added a schematic of transition pathways of peaks 1-3 as the new Fig. 4d and a discussion in the main text (Page 8 Line 259-261 & Line 270-275) as follow:

"The population of D_0^+, as indicated by the intensity of Peak 1, exhibits similar increasing features to the above results, confirming that Peak 1 reflects a charge injection process through the bleaching of D_0^+ ground-state.[22]"..."The energy alignment between electrode and single molecule is shown in Fig. S16. Owing to the small energy offset of the T_1^{2+} β orbital (SUMO+2), which lies 0.21 eV below the Fermi level, electron injection can occur and form Q_0^+ at V_{probe} = 0.2 V (**Fig. 4d**). In contrast, the LUMO+1 of the S_0^{2+} state is 0.48 eV below the Fermi level, and thus Peak 3 is attributed to the S_0^{2+} contribution, corresponding to the transition from S_0^{2+} to the D_n^+ state as summarized in **Fig. 4d**."

(4) Regarding the capture of transient fractional charge states, we are not able to resolve it due to the limitation of our theoretical tools. To realize that purpose, a TDDFT combined with NEGF method is on demand to include the impact of electrode and molecule coupling. We notice that the theoretical method used in ***Sci. Adv.*** 2023, 9, eadf4170, where they can capture the transient electronic structure of a carbon nanotube electron emitter would be a solution for that. However, It is beyond our capability at this moment. The focus of nonequilibrium states in single-molecule junctions just starts in recent years which requires the joint efforts from theorists in the community to understand the phenomena in depth. To emphasize the limitation of our work, we have added a discussion in the main text (Page 10 Line 334-338) as follow:

"Our approach establishes a new experimental route to access nonequilibrium states in charge transport through single-molecule junctions. Fully understanding the underlying mechanisms will require close collaboration with the theoretical community and the development of new frameworks to capture the transient electronic structure of these systems[51, 52]."

New references have been added:

Ref. 47: "Perrin M. L., Verzijl C. J. O., Martin C. A., Shaikh A. J., Eelkema R., van Esch J. H., *et al.* Large tunable image-charge effects in single-molecule junctions. *Nat. Nanotechnol.* **8**, 282

(2013)."

Ref. 50: "Imada H., Imai-Imada M., Miwa K., Yamane H., Iwasa T., Tanaka Y., *et al.* Single-molecule laser nanospectroscopy with micro–electron volt energy resolution. *Science* **373**, 95 (2021)."

Ref. 51: "Li C., Guan M., Hong H., Chen K., Wang X., Ma H., *et al.* Coherent ultrafast photoemission from a single quantized state of a one-dimensional emitter. *Sci. Adv.* **9**, eadf4170 (2023)."

Ref. 52: "Chen S. G., Kwok Y., Chen G. H. Time-dependent density functional theory for open systems and its applications. *Acc. Chem. Res.* **51**, 385 (2018)."

2. Transport data

Comment 1-2: The charge stability diagram in Fig. 2b suggests that at VG = –2.5 V, the conductance onset occurs around VSD =±0.2 V. However, in the pulsed spectrum shown in Fig. 2c, the signal in this voltage range appears less distinct compared to the excited-state resonance at –0.7 V. I understand that pulsed measurements have different noise characteristics, but could the authors comment on the visibility of the ground-state transport channel in the pulsed setup?

Reply 1-2: Thanks for your comment. The primary reason is likely due to the reduced signal-to-noise ratio (SNR) inherent to the pulsed measurements compared to DC measurements, which leads to the absence of the peak at V_{SD} = ±0.2 V (should be ±0.1 V according to our raw data) under pulsed conditions (V_G = –2.5 V). To illustrate this, we have replaced Fig. S9 to include the pulsed *I*-*V* curves with corresponding error bars. As shown in Fig. S9, the noise level in the low-voltage region may hinder the resolution of this spectral feature.

Furthermore, it is important to note that the pulsed differential conductance characteristics is much complicated compared to the conventional differential conductance measurement, due to the formation and decay of excited species highly sensitive to the pulse duration. As presented in Fig. S10c, we observed a significant relaxation feature in the measurements of pulse width variation. That indicates the complete recovery of stabilization, which requires hundreds of nanoseconds learned from ***Science*** 2021, 373, 452, where they probed the triplet quenching dynamics by varying pulse width.

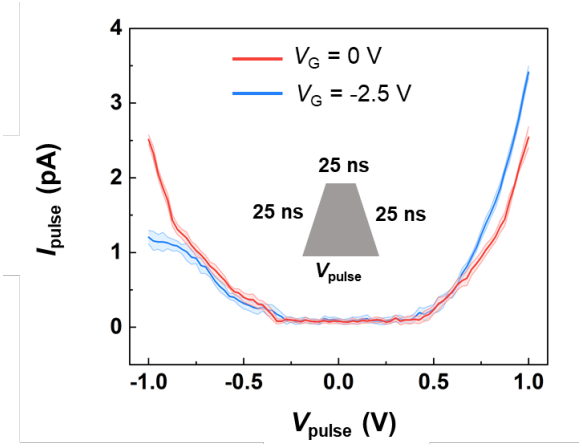


Fig. S9 Pulse current-voltage characterizations at N–1 (blue line, V_G= –2.5 V with the error range indicated by the blue shaded area) and N (red line, V_G= 0 V with the error range indicated by the red shaded area) states of BP molecule.

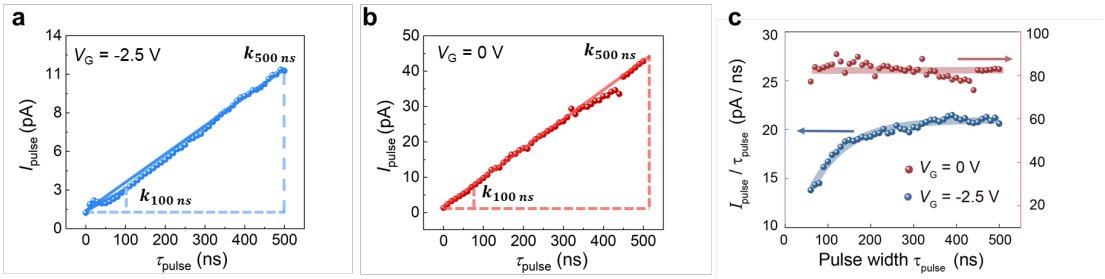


Fig. S10 Single-pulse measurement of the charged single molecule by pulse-width dependence experiment. a,**b**, Measured pulse current I_{pulse} as a function of pulse width τ_{pulse} with fixed –0.8 V amplitude at V_G= –2.5 V (**a**) and 0 V (**b**). **c**.The normalized pulse current by variable pulse width voltage at V_G = –2.5 V (blue line) and 0 V (red line). The red and blue lines are guides for the eye. The normalization method was to extract the slope of the signal difference under different pulse widths compared to that at τ_{pulse} = 0 ns.

To clarify the distinction between constant *I-V* measurement and pulsed *I-V* measurement, we have added a discussion in the main text (Page 3 Line 106-111) as follow:

"Compared with the DC measurement, the absence of the peak at V_{SD} = ± 0.1 V and V_G = –2.5 V under pulsed measurement may originate from the reduced signal-to-noise ratio as evidenced by the raw pulsed *I*–*V* data shown in **Fig. S9**. Additionally, the relaxation of transient species, which is highly sensitive to the pulse duration, may further affect the differential conductance, as revealed by the pulse-width-dependent current measurements (**Fig. S10**)."

3. Technical details and presentation

Comment 1-3: Fig. 2d inset: In the schematic illustrating the pump excitation process, both the lower and upper energy levels are labeled as D0+. Since the pump pulse excites the molecule to a different charge state, labeling the excited level as the ground state D0+ is confusing and appears to be a typo.

Reply 1-3: Thanks for your comment. The excited level labeled as D_0^+ we consider is not a typo. The inset indicates that the D_0^+ is set to an energy situation which can decay and populate the triplet and singlet state, this scenario had been introduced in some AFM works by Prof. Jascha Repp (***Science*** 2021, 373, 452; ***Nat. Nanotechnol.*** 2025, 20, 27). To make it clear, we have replaced it with a new illustration by removing the D_0^+ in the inset and added a new discussion in the caption of **Fig. 2d**:

"The inset illustrates that the D_0^+ can be set to a virtual state (dashed line) with high energy being able to populate the excited states in other charge states."

In addition, we have modified the discussion in the main text (Page 4 Line 115-118) as follow:

"When pump voltage is high enough to interact with the single molecule, it triggers the charge transition as well as the formation of excited states in new charged state[18, 22, 29]. After the formation of charge state, the excited state changes continuously due to the experimental dissipation and recovers to the initial charge state. "

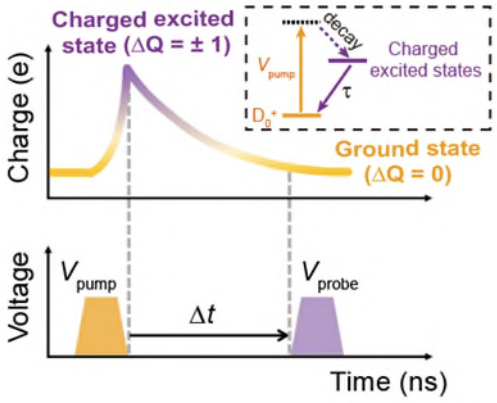


Fig. 2d Schematic representation of relaxation dynamics in pump-probe measurements. $\Delta Q = 0$ indicates the initial charge state as ground state. The $\Delta Q = +1(-1)$ indicates injecting one hole (electron) from the single molecule. The inset illustrates that the D_0^+ can be set to a virtual state (dashed line) with high energy being able to populate the excited states in other charge states.

Comment 1-4: Energy scale in Fig. 3b: It would be helpful to state explicitly whether the y-axis ("E") represents the absolute energy relative to vacuum, or energy relative to the Fermi level.

Reply 1-4: Thanks for your comment. The energy scale (E) in Fig. 3b refers to the absolute energy relative to the vacuum level. Accordingly, we have updated the figure caption to explicitly state: "The y-axis (E) represents the absolute energy relative to the vacuum level."

Comment 1-5: Citations/cross-references: There appears to be a cross-referencing inconsistency where the text mentions "section S7", while the Supplementary Information currently contains sections only up to Section IV. Please check and correct the section numbering.

Reply 1-5: Thanks for your comment and sorry for the mistake, we have made thorough corrections in the revised version, please see the corrections highlighted in the main text and the supplementary information.

Reviewer #2 (Remarks to the Author):

Zhang et al. developed an electronic pump-probe method to access different electronic states of a single-molecule transistor, similar to pump-probe methods used in scanning probe microscopy. Using a pump-probe scheme, they observe three clear signals, of which two have a time-dependency on a timescale of a few 100 ns, indicating transitions into different electronic states.

Comment 2-1: As an expert in scanning probe microscopy, I do not see that the work adds new insights to the understanding of excited-state dynamics. The authors correctly cite the relevant scanning probe microscopy works, in which excited-state energies and lifetimes can be accessed. Incorrectly the authors state that 'the excited state dynamics of open-shell radical remains inaccessible due to the lack of appropriate external gate in STM configuration'. Yes, there is a lack of external gate in STM, but nevertheless open-shell radicals can be studied, as in reference 39. In addition, in AFM on thick insulating films, a gate voltage is applied, allowing the access to different open-shell configurations, see e.g. reference 22. Indeed, in a single-molecule transistor you can apply a gate and source-drain voltage, which might have advantages over scanning-probe microscopy, but these advantages are not apparent from the current work. I do therefore believe that this work is not suitable for Nature Communications.

Reply 2-1: We highly appreciate the reviewer's detailed review and useful suggestions, which help us improve the quality of our work. However, we can not agree with the comment on our novelty. We realized some of our statements may lead to misunderstanding. Compared with the SPM studies, we think we have made two major advances.

1. Electrostatic potential control of lifetime. In the original manuscript, we have demonstrated that the dynamics are highly dependent on the gate voltage, as evidenced by the complete absence of dynamic signals at V_G = 0 V. Following your suggestion to highlight the utility of the gate electrode, we further performed the gate control of lifetime in a new device and added the data in **Fig. S13**. We observe the relaxation dynamics appears when the gate voltage is approaching the resonance transport, and the lifetime saturates when the charge state is stabilized in the Coulomb blockade regime (**Fig. S13d**). The non-steplike gate-dependence near the state cross point demonstrates that the electrostatic potential change can effectively control the lifetime of excited states in a single molecule. We have added a discussion in the main text (Page 4) as follow:

"Moreover, we realize the control of relaxation dynamics by using gate voltage to control the energy level alignment in device 3 of **BP** (**Fig. S13**). This demonstrates that the gate coupling provides direct electrostatic control of molecular relaxation dynamics, independent of transport bias."

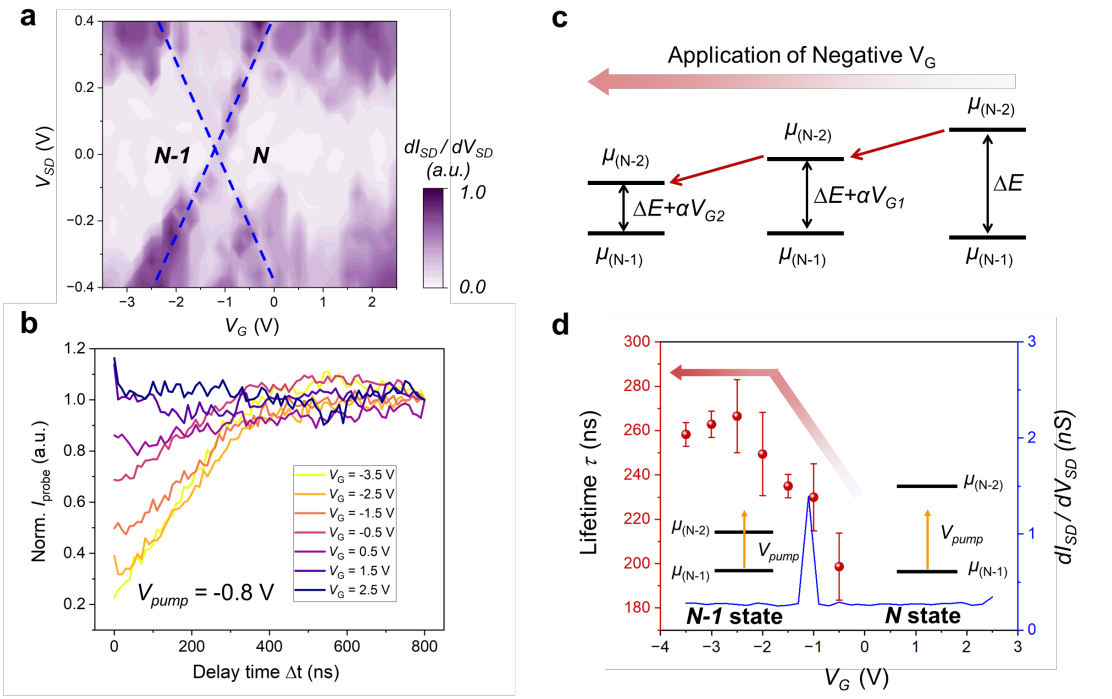


Fig. S13 All-electronic pump-probe measurements of the BP molecule in device 3. (**a**) Charge stability diagram of device 3 showing the differential conductance (dI_{SD}/dV_{SD}) as a function of bias voltage (V_{SD}) and gate voltage (V_G) at 30 K. (**b**) Corresponding dependence of the probe current I_{probe} on the delay time as a function of gate voltage $V_{gate.}$ at a fixed pump voltage $V_{pump} = -0.8$ V. (**c**) Many-body energy diagram illustrating gate-induced modulation, in which the energy gap between the *N*−*1* and *N*−*2* states decrease as a negative gate voltage V_G applied. (**d**) Differential conductance (dI_{SD}/dV_{SD}) at $V_{SD} = 0$ V (blue line) and the lifetime of electrically excited states (red dots) as a function of continuous gate voltage V_G. The peak around $V_G \approx -1$ V in the differential conductance indicates the transition from the N state to the *N*−*1* state. Correspondingly, the transient dynamics become pronounced at $V_G < -1$ V, since the population of the *N*−*1* state is negligible for $V_G > -1$V. The initial increase in the lifetime with increasing V_G is attributed to the reduction of the energy gap between the *N*−*1* and *N*−*2* states induced by gate modulation, allowing the fixed pump voltage V_{pump} to gradually reach and exceed this energy separation.

2. Effective coupling between electric field and dipole moment of excited states. We should emphasize the key difference between our system and SPM is the coupling between electric field and dipole moment shown in **Fig. R1**. In SPM configuration, the molecule lies on substrate with or without an insulator. For planar molecule, the dipole moment is orthogonally aligned with the electric field, suggesting extremely weak coupling. However, in our system, the dipole moment is parallelly aligned with the electric field, suggesting strong coupling. Therefore, the presence of pump voltage is able to induce huge energy shift by coupling with the dipole moment in single-molecule junctions as discussed in many papers studying electric field effects on single-molecule junctions (*e.g.* ***Nat. Chem.*** 2016, 8, 1091).

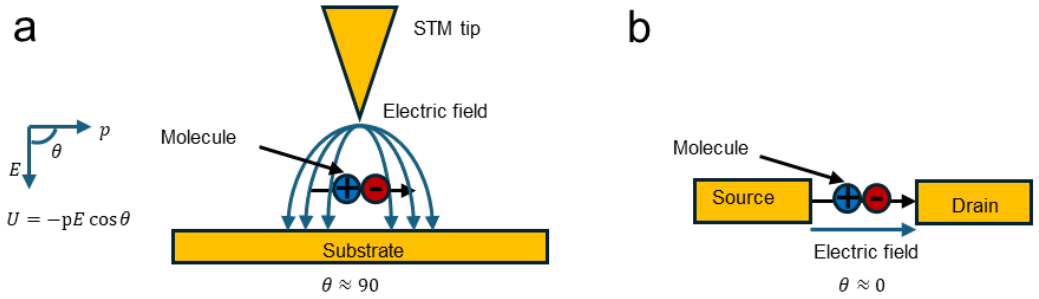


Fig. R1 Electric field coupling with molecular dipole moment in STM (**a**) and single-molecule junction (**b**).

The evidence of the strong coupling between electric field and excited states in our system is presented in **Fig. R2**, along with the previous results from Prof. Jascha Repp's work as a reference (***Nat. Nanotechnol.*** 2025, 20, 27). There is no obvious energy shift in their transient electronic spectra (**Fig. R2a**). Another example is from Prof. Yousoo Kim, they observed a very tiny energy shift of hundreds of microelectron volt driven by the electric field (**Fig. 4** in ***Science*** 2021, 373, 95). Several transient differential conductance spectra from our results clearly show that the excited states shift at different delay time (**Fig. R2b**). This is due the strong coupling between electric field at the presence of pump voltage and the difference dipole moment of S_0^{2+} and T_1^{2+} which are -14.20 Debye and -11.64 Debye as presented in **Table S2**.

[FIGURE REDACTED]

Fig. R2 Transient electronic spectra. (**a**) **Fig .4d** in ***Nat. Nanotechnol.*** 2025, 20, 27. (**b**) Our results shown in **Fig. S21**.

Table S2 Calculated dipole moments of N, N–1 and N–2 states. The **BP** molecule geometries are optimized under different external electric fields (E = 0.8 V and 0 V).

E	N state (S_0)	N–1 state (D_0^+)	N–2 state (S_0^{2+})	N–2 state (T_1^{2+})
0.8 V	-5.12 Debye	-14.37 Debye	-14.20 Debye	-11.64 Debye
0 V	0 Debye	0 Debye	0 Debye	0 Debye

To clarify this point, we have added a discussion in the main text (Page 9 Line 302-321 & Page 10 Line 315-324):

"We first excluded structural change induced by charge injection or electric fields through DFT

analysis (**Fig. S17**), which showed minimal orbital energy perturbations (<0.1 eV) from geometric modifications. However, the strong external electric field in single-molecule junction (~10^8 V/m) in the presence of pump pulse could also theoretically modify excited-state energies by coupling with the dipole moment[24, 48, 49]. The calculated dipole moment (**Table S2**) suggests that the coupling strength of D_0^+ and S_0^{2+} is almost same. However, the coupling strength of T_1^{2+} is significantly smaller, supporting the initial energy splitting is caused by the difference of coupling strength. Therefore, the converging trajectories of Peak 2 and 3 in Fig. 4e (eventually merging at +0.69 V after 200 ns) strongly suggest these features trace the non-equilibrium dynamics of redox during *N–2→N–1* state transition."

"Meanwhile, the evolution of the energy gap between S_0^{2+} and T_1^{2+} points to a state-specific relaxation: the initial 220 meV gap may be amplified by the rapid stabilization of the T_1^{2+} state relative to S_0^{2+} due to their differing dipole moments. This phenomenon is exclusively observed in single-molecule radical junctions where charge transport is parallel to the molecular backbone direction, enabling enhanced many-body coupling between transient charges and molecular orbitals. An example in STM study shows that the orthogonal coupling between electric field and molecular dipole only induces a microelectronvolt shift[50]."

Besides, to clarify the above points, we have also modified the introduction (Page 2 Line 41-51) as follows:

"The state-of-the-art studies of electronic pump-probe coupled scanning probe microscopy (SPM) offer promising insights into non-equilibrium quantum transport with nanosecond time resolution[17-22]. These techniques provide a powerful platform for probing transient dynamics mediated by electrically induced excited states in single-molecule tunnel junction that are weakly coupled to their environment. However, the orthogonal alignment between electron transport direction and dipole moments of excited states renders the weak electric-dipole interaction, which is essential for electrically controlling the intramolecular interactions of excited states. In single-molecule transistors, the electric field is parallel to the dipole of molecule leading to strong interaction[23-28]. The external gate potential provides additional electrostatic field to control the charge state and dynamics of single molecule."

My main criticism of the current work is in the interpretation of their data. The authors make various claims, of which some seem incorrect and others are not properly supported:

Comment 2-2: Line 166 'The long lifetime also supports the involvement of spin flipped state, i.e. triplet state'. Indeed, spin-forbidden transitions have a long lifetime. However, it seems from this paper that the authors are probing charge transitions and not the transition from the excited triplet state into the ground singlet state. In that case, the different time scales could be explained by different tunneling rates and are not dependent on the lifetime of the excited state, but on the lifetime of the charged states.

Reply 2-2: Thanks for your comment. In our case, the relaxation is governed by the competition between charge transition (*e.g.*, $T_1^{2+} \longrightarrow D_0^+$) and intrinsic de-excitation (*e.g.*, $T_1^{2+} \longrightarrow S_0^{2+}$). The reason to believe that our observation includes both relaxation channel is based on the non-step-like voltage-dependence of lifetime. If the lifetime were determined solely by charge tunneling rates without the involvement of coherent interaction between different excited states, the voltage dependence would exhibit a characteristic step-like behavior in the dependence between lifetimes

and pump voltage. As presented in **Fig. R3** from ***Phys. Rev. Lett.*** 2021, 126, 176801, the energy space between each state in NPc^0 is large enough to avoid interstates interaction and similar to the pure charge transition process. The lifetime against probe voltage exhibits a step-like function based on the fact the excitation of T_1 makes little impact to S_0. Our data revealed a clear non-step-like evolution around –0.8 V (**Fig. R4**), thereby indicating the interplay between two transition channels (charge transition and de-excitation).

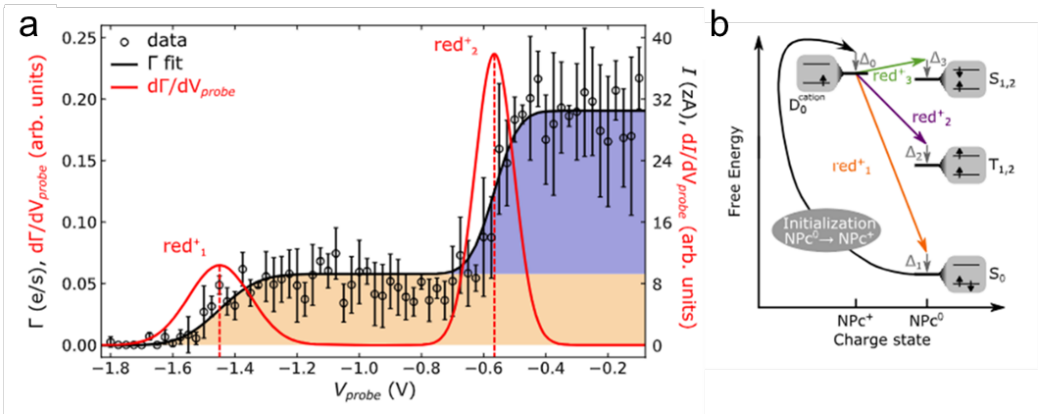


Fig. R3 (**a**) Lifetime analysis of the $NPc^+ \rightarrow NPc^0$ transition as a function of V_{probe} (**Fig. 3a** in ***Phys. Rev. Lett.*** 2021, 126, 176801). (**b**) Many-body electron picture associated with the measured charge-state transitions (**Fig. 4d** in ***Phys. Rev. Lett.*** 2021, 126, 176801).

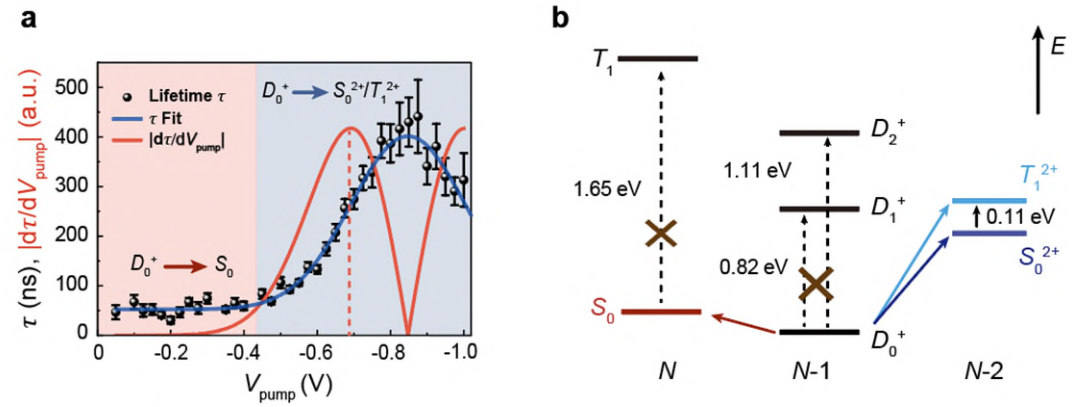


Fig. R4 (**a**) Lifetime analysis of the $BP^+ \rightarrow BP^{2+}$ and $BP^+ \rightarrow BP^0$ transition as a function of V_{pump} (**Fig. 3a** in main text). (**b**) Many-body electron picture associated with the measured charge-state transitions.

We realized our statement that "The long lifetime also supports the involvement of spin flipped state, i.e. triplet state" might lead to misunderstanding. Accordingly, we have reorganized the discussion regarding the lifetime in main text (Page 6 Line 174-178):
"Interestingly, the non-quantized correlation between lifetime and pump voltage around V_{pump} = –0.8 V is distinct from the quantized excited state dynamics in an individual naphthalocyanine molecule where the lifetime against the voltage exhibits the plateau-like feature[39]. Such a discrepancy suggests the appearance of coherent transition between multiple excited states."

Comment 2-3: The authors assign the observed peak in Fig. 3 to the S02+ and T12+ states. They

are close in energy, so it could be that they are indeed both accessed. The authors do not explain well why they assign the peak drop to accessing the T12+ state (I would have naively assumed the peak itself is then due to accessing both S02+ and T12+). In other words, why is the S02+ a low-conductance state and the T12+ a high conductance state, as the authors write?

Reply 2-3: Thank you for raising this important point. We would like to clarify that the feature observed in **Fig. 3** is simply not a resonant peak. As we response in **Reply 2-2**, if the signal was solely due to accessing a single state, the lifetime or current would exhibit a characteristic plateau-like evolution. Instead, the observed increase/drop feature indicates a competitive interplay between two energetically proximal states with distinct transport properties (corresponding to a high-conductance state and a low-conductance state, ***Nature*** 2008, 453, 633).

The assignment of the lifetime rise to accessing S_0^{2+} and the peak drop to accessing T_1^{2+} state is mainly obtained by TDDFT calculation in **Fig. 3b**. After excluding states like T_1 state (due to energy mismatches) and D_n^+ (due to the requirement of multi-electron process and the estimated short lifetime derived from the Einstein equation), the S_0^{2+} and T_1^{2+} states remain the only viable candidates. Our calculations confirm that they are close in energy (T_1^{2+} being slightly higher), leading to the observed features. Regarding the conductance difference, while we cannot directly measure the intrinsic conductance of these transient states, our TDDFT results suggest that the orbitals of the T_1^{2+} states are energetically closer to the Fermi level compared to those of S_0^{2+}. This alignment should imply a higher tunneling probability (higher conductance) for the T_1^{2+} states.

To clarify this point, we have removed the direct assignment that the S_0^{2+} and T_1^{2+} states as low- and high-conductance to avoid misleading.

Accordingly, the revised discussion in the main text is:

"The incoherent transition at $V_{pump} > -0.4$ V corresponds to the electron injection to the singly unoccupied molecular orbital (α-SUMO) illustrated in **Fig. 3c**, enabling the transition from D_0^+ to S_0. Before reaching the energy level of singly occupied molecular orbital (α-SOMO and β-SOMO), the dynamics exhibit a flat trend caused by S_0. At Vpump around −0.6 V, the S_0^{2+} state gradually increases to be the dominant state, resulting from the removal of one electron from SOMO. As Vpump < −0.8 V, reaching the energy level of α-SOMO, the T_1^{2+} state replaces S_0^{2+} to be the dominant state. The shift in the branching ratio of transitions into S_0 and S_0^{2+}/ T_1^{2+} leads to the observed increase in τ with pump voltage.

Based on the TDDFT results, we mapped the energy alignment of both states relative to the Fermi level in **Fig. S16**, which reveals that the orbitals associated with T_1^{2+} are energetically closer to the Fermi level compared to those of S_0^{2+}. This closer proximity implies a higher tunneling probability for T_1^{2+}, which accounts for Gaussian-shaped I_{probe} regime around $V_{pump} = \pm 0.8$ V in **Fig. 2f**."

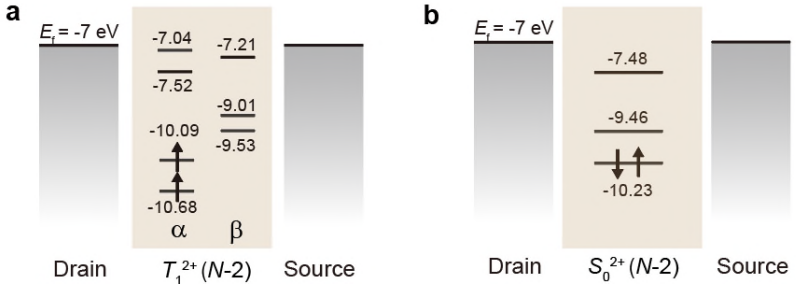


Fig. S16 Single-particle illustration of energy alignment between (a) T_1^{2+} and (b) S_0^{2+} with electrodes derived from TDDFT calculations.

Comment 2-4: It is not clearly explained how, by increasing the pump voltage, first a transition into S0 and later a transition into S02+ and T12+ is opened in Fig. 3b. It would be helpful to make the connection between Fig. 3b and the applied pump voltage. Is the pump voltage (times a lever arm) reflected in the length of the arrows? Are the levels itself also shifting when the pump voltage is changed because of the lever arm?

Reply 2-4: Thanks for your comment. The lever arm is a character of the gate electrode with an insulating layer, which likely explains why Prof. Repp *et al.* named the substrate in their Ultrafast-SPM setup as a 'gate' (***Science*** 2021, 373, 452; ***Nat. Nanotechnol.*** 2025, 20, 27). In our single-molecule transistor geometry, the coupling efficiency (α, defining the lever arm of the electrostatic gate) of gate electrode is approximately 0.3 based on the slopes of the Coulomb diamond boundaries. Such a value is in the range of the previous reports using same 10 nm HfO_2 as insulating layer (***Nat. Nanotechnol***. 2024, 19, 986; ***Angew. Chem. Int. Ed.*** 2024, 63, e202401323). However, the scenario of the source-drain connection differs from the SPM configuration due to the strong coupling between the molecule and the electrodes. In this regime, the effective bias lever arm is essentially unity (~1). Such a value could also be verified from the STM-Induced Electroluminescence in a strong coupled single-molecule junction (***Phys. Rev. Lett***. 2016 116, 036802). As present in **Fig. R5**, the applied voltage of 1.56 V could lead to the photon emission with 1.543 eV.

In the junctions of our work, co-tunneling processes enable simultaneous electron tunneling from the source to the molecule and from the molecule to the drain (***Chem. Soc. Rev.*** 2015, 44, 902). This process is activated when the voltage is at least equal to the energy difference between the excited state and the ground state. Therefore, the lever arm in our system is approximately 1.

[FIGURE REDACTED]

Fig. R5 Figs. 2 & **4** in ***Phys. Rev. Lett.*** 2016 116, 036802.

To clarify this point, we have added a discussion in the main text (Page 8 Line 250-252):
"Their central energies are determined from the probe voltage, which directly reflects the energy of each state via the cotunneling mechanism with a lever arm close to unity[29]."

Comment 2-5: I am also very surprised that the transition from D0+ into S0 doesn't show a clear resonance, but the one into S02+ and T12+ does, maybe because the transition to S0 is opened all the time? In addition, it seems that the signal being measured is a time-average over a single molecule, which could explain the increase in tau with pump voltage by altering the ratio of tunneling into S0 vs S02+/T12+, which seem to have a lower tunneling rate to decay back to D0+.

Reply 2-5: Thanks for your comment. As we responded in **Reply 2-2** and **Reply 2-3**, the opening of a simple transition channel to a new state typically manifests as a plateau-like feature. We agree the reviewer's opinion that the transition to S_0 remains accessible ("opened") throughout the measurement, resulting in a plateau-like lifetime (or I_{probe}) evolution. In fact, accessing the S_0 state requires a finite threshold voltage. As observed in the normalized I_{probe} at Δt = 0 ns under different V_{pump} excitation (**Fig. R6**), the conductance plateau exhibits a falling edge within the pump voltage range of ~±0.1 V, which is consistent with the resonance value of ±0.1 V in the charge stability diagram at V_G = –2.5 V.

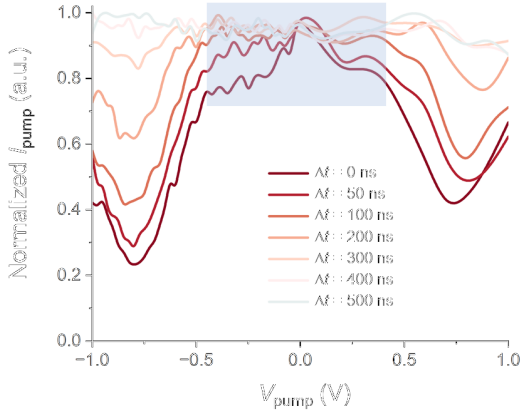


Fig. R6 Normalized I_{probe} traces as a fucnction of V_{pump}, extracted from **Fig. 2e** for different value of Δt.

However, we would like to clarify that the Gaussian-shaped feature observed in the dependence of lifetime (or I_{probe}) by the pump voltage does not constitute a conventional resonance behavior. As established by Gross *et al.* (***Phys. Rev. Lett.*** 2021, 126, 176801), the true resonance energy should be determined from the central energy of the first-order derivative (**Fig. R7**), Consequently, the distinct Gaussian-shaped feature that emerges at higher pump voltages represents a significant deviation from the standard plateau-like behavior expected for the opening of a single state. This anomalous non-monotonic evolution leads us to attribute the signal to the competitive interplay between energetically proximal states, particularly since the observed lifetime evolution is inconsistent with the plateau-like trends.

[FIGURE REDACTED]

Fig. R7 (**a**) Lifetime analysis of the in **Fig. 3a** in ***Phys. Rev. Lett.*** 2021, 126, 176801 and (**b**) our results in **Fig. 3a** in the main text.

To substantiate this point, we also performed a derivative analysis ($d\tau/dV_{pump}$) following the cited reference and identified the resonance center in the updated **Fig. 3a**. Accordingly, we have added the following discussion to the main text (Page 5 Line 164-178):

"The central energy of its first order derivative indicates the resonance energy of -0.68 eV associated with the excited state, which is consistent with the resonance position observed in the single-pulse differential conductance spectrum. Notably, prior to reaching this resonance energy, we observe a fast decay component with a lifetime of ~68 ns that exhibits a plateau-like feature. This indicates that one non-equilibrium state is accessible even at low applied voltages. We attribute this behavior to the gate voltage being tuned near the charge degeneracy point (cross point) of the *N* and *N-1* states[37], where a slight voltage applied can trigger the charge filling and the charge transition is expected to be faster. Therefore, we attribute the short lifetime plateau observed in the low pump voltage regime to the formation of S_0[38]. Interestingly, the non-quantized correlation between lifetime and pump voltage around V_{pump} = -0.8 V is distinct from the quantized excited state dynamics in an individual naphthalocyanine molecule where the lifetime against the voltage exhibits the plateau-like feature[39]. Such a discrepancy suggests the appearance of coherent transition between multiple excited states."

New references has been added:

Ref. 37: "Lau C. S., Sadeghi H., Rogers G., Sangtarash S., Dallas P., Porfyrakis K., *et al.* Redox-dependent franck-condon blockade and avalanche transport in a graphene-fullerene single-molecule transistor. *Nano Lett.* **16**, 170 (2016)."

Ref. 38: "Fujisawa T., Austing D. G., Tokura Y., Hirayama Y., Tarucha S. Allowed and forbidden transitions in artificial hydrogen and helium atoms. *Nature* **419**, 278 (2002)."

Comment 2-6: Line 210-212: 'In contrast to the single-pulse differential conductance spectra, two new resonant peaks (Peaks 2 & 3) appear in the positive probe voltage regime, indicating they are transient species generated by excited states after the pump pulse.' Do the authors here refer to Fig. 2c? There is a clear shoulder at 0.5 to 1.0 V, which indicates that these signals are already present there. The authors also see them at 0 delay time in Fig. 4a. Thus, it is not clear to me why they are only generated after the pump pulse, as the authors claim.

Reply 2-6: Thanks for your comment. To clarify the origin of these signals, we compare the single-pulse spectrum (**Fig. 2c**) with the transient spectrum (**Fig. S16**, corresponding to the line profiles in **Fig. 4a**). As evident from this comparison in **Fig. R8**, Peak 2 (specifically observed at ~0.2 eV at 0 ns delay**)** is not discernible in the single-pulse differential conductance spectrum (top panel of **Fig. R8**). Furthermore, while a broad shoulder exists in top panel of **Fig. R8**, the new features emerging after the pump pulse (Peaks 2 and 3) manifest as distinct peaks rather than a shoulder. This morphological difference indicates that Peaks 2 and 3 are indeed transient species generated by the excited states rather than intrinsic features of the ground state.

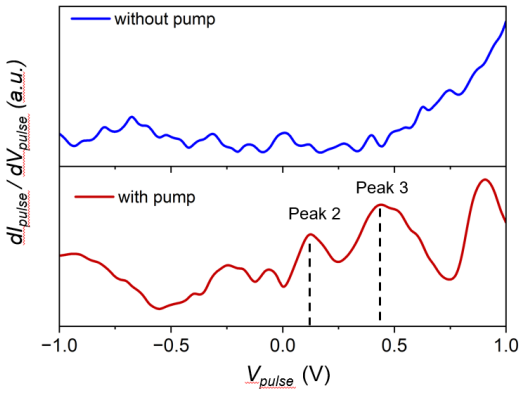


Fig. R8 The differential conductance derived from I_{probe}-V_{probe} curves using single-pulse measurement (without pump, top panel, **Fig. 2c** in the main text) and pump-probe measurement (Δt = 0 ns, with pump, lower panel, **Fig. 4c** in the main text).

To emphasize this point, we have added a discussion in main text (Page 8 Line 262-268):
"In contrast to the single-pulse differential conductance spectra (**Fig. 2c**), Peak 2 (~0.2 eV at 0 ns) and Peak 3 (~0.5 eV at 0 ns) appear exclusively after the pump pulse. Although a spectral feature exists in this energy range in **Fig. 2c**, the transient signal manifests as a distinct peak rather than the broad shoulder observed in the steady state spectra. Moreover, Peak 2 and Peak 3 decay with delay time (**Fig. 4c**). These distinctions confirm that Peaks 2 and 3 represent transient species generated by excited states following the pump pulse."

Comment 2-7: I got very confused by comparing Fig. 2e (please mention there in the caption the used probe voltage) and Fig. 2f, especially since Fig. 2e only shows negative pump voltage and not positive ones. The authors do not properly explain the different effects of the pump and probe pulse, making it challenging to interpret these two plots. I think it would have been very helpful to explain first in more detail what only the pump pulse does. Is there for instance a dependence on the pulse width of the pump pulse?
Reply 2-7: Thanks for your comment. Regarding the dynamics of the positive pump regime, we have updated **Fig. 2e** to explicitly show the dependence of the probe current on the delay time as a function of pump voltage for both positive and negative pump pulses. The general dynamic phenomena appear similar under both direction of pump pulse. And we noticed a difference in their lifetimes. We now attribute to the nature of the excited states identified in the dI/dV spectrum (**Fig. 2c**): the negative bias excites a discrete state (corresponding to the sharp peak at –0.65 V) with a low dephasing rate, whereas the positive bias excites a continuum state (corresponding to the broad shoulder at 0.5–1.0 V) characterized by a much higher dephasing rate. We have revised the manuscript to explicitly discuss these distinct effects and their correlation with the observed lifetimes in main text (Page 4 Line 130-133):
"A reduced current regime with a lifetime of hundreds of nanoseconds appears when the pump voltage is set around V_{pump} = ±0.8 V, indicating the formation of transient species. The trigger voltage is consistent with the resonant peak and shoulder in pulsed differential conductance spectroscopy in **Fig. 2c**. The lifetime under V_{pump} = +0.8 V is notably shorter than that under V_{pump} = -0.8 V. This indicates that the negative bias excites a discrete state (corresponding to the sharp peak at -0.65 V

in **Fig. 2c**) with a low dephasing rate, whereas the positive bias excites a continuum state (corresponding to the broad shoulder at 0.5–1.0 V in **Fig. 2c**) exhibiting a much higher dephasing rate."

Regarding the comparison between **Fig. 2e** and **Fig. 2f** in previous submission, we would like to clarify that these figures are not intended for direct comparison, as they represent distinct experimental domains. To prevent confusion, we have made the following revisions:

1. We have revised the manuscript structure to separate them: **Fig. 2** now focuses exclusively on the pump excitation mechanism, utilizing a fixed probe voltage to compare the conductance changes induced by different pump triggers. We also updated the figure to present the raw data instead of normalized traces. In the absence of a pump pulse, the probe current remains at a constant level of approximately I_{probe} = 1.2 pA, which serves as a reference baseline. Consequently, the current deviation observed relative to this baseline after the pump excitation reflects the dynamical evolution of the transient states. **Fig. 4** focuses on the probe spectroscopy, which presents the transient *I-V* spectra measured after a specific pump excitation, revealing the specific transport features of the excited states.

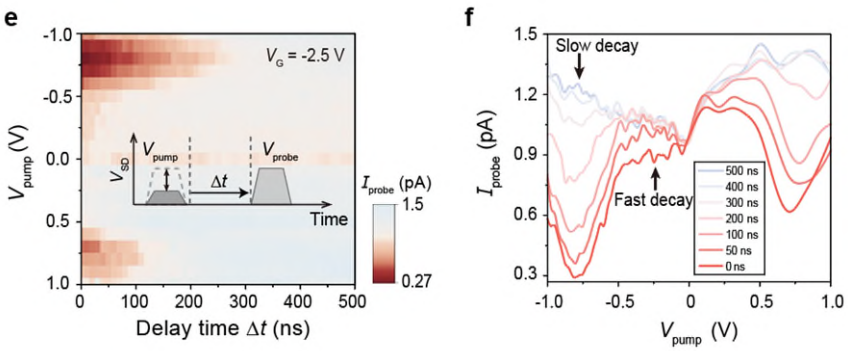


Fig. 2 (**e**) Corresponding dependence of the probe current I_{probe} on the delay time Δt as a function of pump voltage V_{pump} at a continuous V_G = –2.5 V. (**f**) Selected I_{probe} traces as a fucnction of V_{pump}, extracted from (**e**) for different value of Δt.

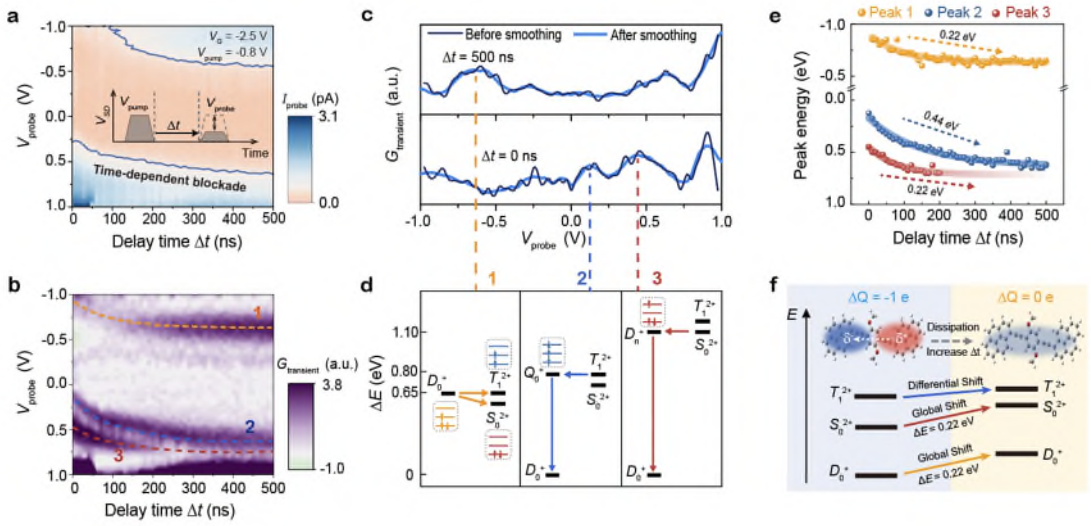


Fig. 4 Transition pathways and Coulomb interaction among excited states. (**a**) Corresponding dependence of the probe current I_{probe} on the delay time as a function of probe voltage V_{probe} after a fixed pump voltage V_{pump} = –0.8 V at a continuous V_G = –2.5 V. (b) Transient differential conductance spectroscopy derived from (**a**). Each differential conductance curve is smoothed with a Savitzky–Golay filter with a window length of 11 for better recognition. (**c**) Selected differential conductance (right panel) derived from I_{probe}-V_{probe} curves (left panel) before (black) and after (blue) smoothing at Δt = 0 ns (lower panel) and 500 ns (up panel). (**d**) Schematic of transition pathways of peaks 1-3. Peak 1 appears at long delay times, where the population of the D_0^+ state is higher, and is therefore attributed to a re-excitation process involving transitions from D_0^+ to S_0^{2+}/ T_1^{2+}. Peak 2 originates from the contribution of the T_1^{2+} state and corresponds to the transition from T_1^{2+} to Q_0^+. Peak 3 corresponds to the transition from S_0^{2+} to the D_n^+ state. (**e**) Peak energy extracted from (**a**). The lines are guides to the eye. **(f)** Illustration of Coulomb interactions among excited states, including a global energy shift and a differential energy shift during charge dissipation.

2. We have added a schematic diagram in the Supplementary Information (**Fig. S23**) to illustrate the many-body model across the four measurement stages: Gate, Pump, Relaxation (Delay), and Probe. The continuous gate voltage sets the system near the charge degeneracy point, enabling the transition from N state to N-1 state. The Pump pulse serves to trigger the excitation and varying the pump voltage (as in **Fig. 2e**) allows us to determine the energy threshold required to access the excited state. The presented data in **Fig. S10** (previously discussed in the SI) demonstrating the dependence of the signal on the pump pulse width with only pump pulse. During relaxation stage (In delay time stage, bias is equal to 0 V), the excited state undergoes spontaneous relaxation back to the ground state. The Probe pulse is employed to detect the relaxation dynamics of the transient states and varying the probe voltage allows us to map the *I*-*V* characteristics of the transient species (e.g., at Δt = 0 ns, the population of the charged excited state S_0^{2+}/ T_1^{2+} is dominant).

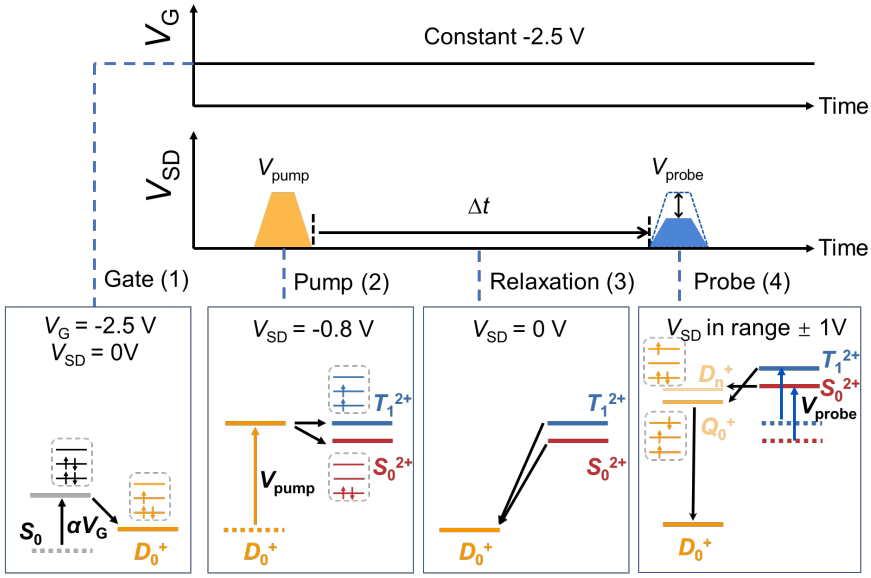


Fig. S23 The role of the four measurement stages: Gate, Pump, Relaxation (Delay), and Probe.

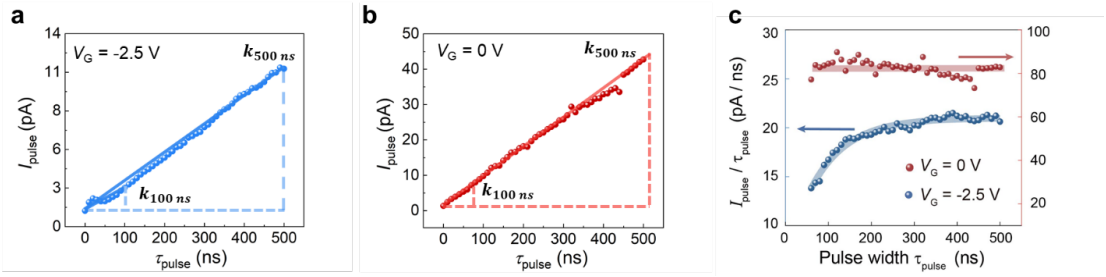


Fig. S10 Single-pulse measurement of the charged single molecule by pulse-width dependence experiment. a,b, Measured pulse current I_{pulse} as a function of pulse width τ_{pulse} with fixed –0.8 V amplitude at V_G= –2.5 V (a) and 0 V (b). c.The normalized pulse current by variable pulse width voltage at V_G = –2.5 V (blue line) and 0 V (red line). The red and blue lines are guides for the eye. The normalization method was to extract the slope of the signal difference under different pulse widths compared to that at τ_{pulse} = 0 ns.

Comment 2-8: Line 217/218: Why do T12+ and S02+ transfer to a Dn+ state and not directly to D0+? If the molecule is in T12+, you can tunnel an electron in the lower level and for S02+ into the first empty level.

Reply 2-8: We thank the reviewer for raising this point and apologize for the confusion. We would like to clarify that the description in Lines 217–218 refers to the probe pulse-induced transitions (corresponding to the resonant peaks observed in **Fig. 4b**), rather than the spontaneous relaxation pathway. Specifically, these peaks arise when the probe current drives the system from the intermediate excited states ($T_1^{2+}$and S_0^{2+}) to higher-lying states (Q_0^+). In the absence of such external probe excitation (refer to the delay stage in pump-probe experiment), these states indeed spontaneously relax directly to the ground state (D_0^+). We have updated **Fig. 1** to include schematic illustrations of these two distinct processes: (i) the spontaneous relaxation of T_1^{2+} and S_0^{2+} into the ground state D_0^+ during the delay stage, and (ii) the probe-induced tunneling transitions from T_1^{2+} and S_0^{2+} to D_n^+ under the applied probe voltage.

To emphasize this point, we have updated **Fig. 4d** to explicitly illustrate the transition pathways for these peaks and add a discussion in main text (Page 8 Line 270-275):

"The energy alignment between electrode and single molecule is shown in **Fig. S16**. Owing to the small energy offset of the T_1^{2+} β orbital (SUMO+2), which lies 0.21 eV below the Fermi level, electron injection can occur and form Q_0^+ at V_{probe} = 0.2 V (**Fig. 4d**). In contrast, the LUMO+1 of the S_0^{2+} state is 0.48 eV below the Fermi level, and thus Peak 3 is attributed to the S_0^{2+} contribution, corresponding to the transition from S_0^{2+} to the D_n^+ state as summarized in **Fig. 4d**."

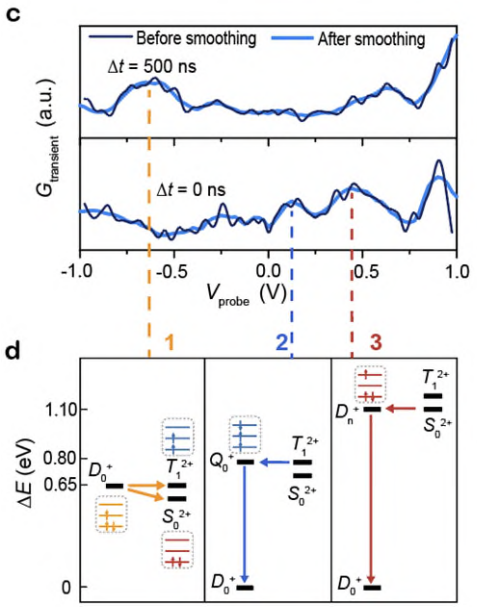


Fig. 4 (**c**) Selected differential conductance derived from panel (**e**) before (black) and after (blue) smoothing at Δt = 0 ns (lower panel) and 500 ns (up panel) (**d**) Schematic of transition pathways of peaks 1-3. Peak 1 appears at long delay times, where the population of the D_0^+ state is higher, and is therefore attributed to a re-excitation process involving transitions from D_0^+ to S_0^{2+}/ T_1^{2+}. Peak 2 originates from the contribution of the T_1^{2+} state and corresponds to the transition from T_1^{2+} to Q_0^+. Peak 3 corresponds to the transition from S_0^{2+} to the D_n^+ state.

Comment 2-9: One of the main claims of the paper is that the energy of the T12+ and S02+ states are changing with the pump-probe delay time. The authors do not support enough evidence for this claim. They write (line 222) 'While there is one possibility the electronic pump-probe technique could theoretically average discrete quantum transition events into smoothed Iprobe-Vprobe responses through repetitive excitation cycles, the observed 220 meV energy resolution (evident in the energy difference between Peak 2 and Peak 3 at t = 0 ns) contradicts this interpretation, as the 440 meV shift of Peak 2 substantially exceeds this resolution limit.' The fact that the energy resolution between the two peaks is 220 meV, doesn't mean that the two peaks cannot represent an average population. Only that the two peaks seem to reflect two independent pathways. I believe that the first part of their sentence is actually giving the right interpretation. They also illustrate this in Fig. 4b, they transfer from T12+ into D0+ and S02+ into D0+. So what if the peak energy they measure is reflecting the average between T12+/S02+ and D0+, and is shifting in energy because of the changing populations?

Reply 2-9: We appreciate the reviewer's critical assessment of our interpretation. We agree that the population dynamics may influence the observed spectral shifts, however, our data suggests a more nuanced dual-mechanism. Specifically, we distinguish between two types of energy evolution:

1. Global Energy Shift: A uniform shift of Peak 1 and Peak3, which we attribute to energy level renormalization driven by the dissipation of total molecular charge.

2. Differential Energy Shift: A time-dependent change in the energy gap between T_1^{2+} and S_0^{2+}. This reflects dynamic changes in the local screening environment and the distinct relaxation pathways of these two states.

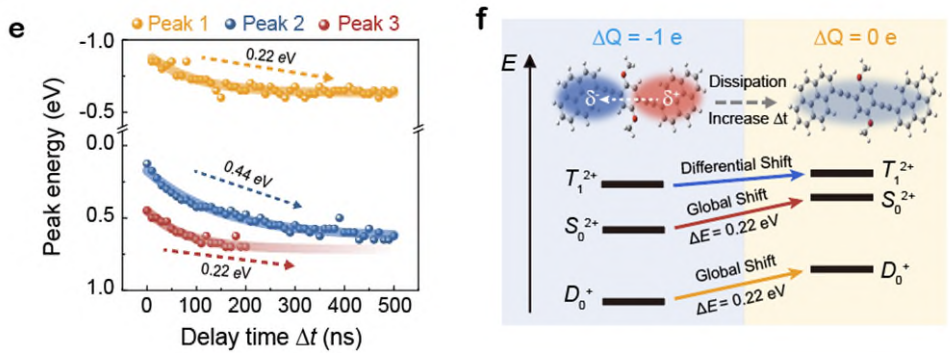


Fig. 4 (**e**) Peak energy extracted from **Fig. 4b**. The lines are guides to the eye. **(f)** Illustration of Coulomb interactions among excited states, including a global energy shift and a differential energy shift during charge dissipation.

By analyzing the peak profiles and the magnitude of the shift, we believe that the continuous peak movement is not merely a population average but reflects a genuine physical evolution of the excited-state landscape. As we responded in **Reply 2-1**, the comparison between a previous result in time-resolved AFM study (***Nat. Nanotechnol.*** 2025, 20, 27) and our results is presented in **Fig. R2a**. Our observation of such a huge energy shift in transient species is inconsistent with the assumption that the population change dominates the energy dynamics (**Fig. R2b**).

[FIGURE REDACTED]

Fig. R2 Transient electronic spectra. (**a**) **Fig .4d** in ***Nat. Nanotechnol.*** 2025, 20, 27. (**b**) Our results shown in **Fig. S21**.

Here, we should emphasize that the key difference between our system and SPM studies is the coupling between electric field and dipole moment (**Fig. R1**). In SPM configuration, the molecule lies on substrate with or without insulator. For planar molecule, the dipole moment is orthogonally aligned with the electric field, suggesting an extremely weak coupling. However, in our system, the dipole moment is parallelly aligned with the electric field, suggesting strong coupling. Therefore, the presence of pump voltage is able to induce huge energy shift by coupling with the dipole moment in single-molecule junctions as discussed in many papers studying electric field effects on single-molecule junctions(*e.g.* ***Nat. Chem.*** 2016, *8*, 1091-1098).

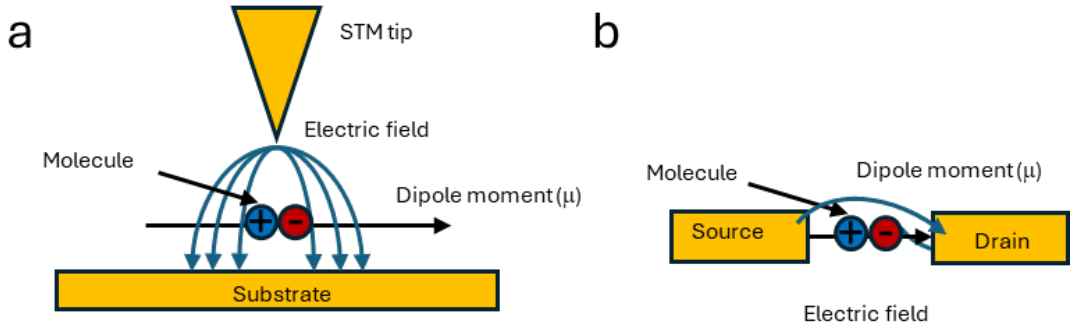


Fig. R1 Electric field coupling with molecular dipole moment in STM (**a**) and single-molecule junction (**b**).

We have revised the manuscript (Page 9 Line 293-301) to clarify these mechanisms.
"The electronic pump-probe technique could, in principle, average discrete quantum transition events into smoothed I_{probe}-V_{probe} responses through repetitive excitation cycles. However, the observed dynamics suggest a more complex origin. We extract the peak energies of them at every delay time presented in **Fig. 4e**. The energy of D_0^+ (Peak 1) and S_0^{2+} (Peak 3) shift synchronously, suggesting the ground states of each redox states is dependent on the global energy shift by Coulomb renormalization[47]. Notably, the energy of S_0^{2+} and T_1^{2+} shifts distinctly with delay time, where the central energies of Peak 2 and 3 exhibit a continuous downward shift of ~ 440 meV and ~220 meV within ~150 ns, respectively. "

Comment 2-10: The authors also claim 'provides direct evidence for meta-stable molecular states with fractional charge occupancy'. I do not see this claim to be justified. It seems the molecule is either 2+ or +, but a time averaged is e.g. showing 1.5+.
Reply 2-10: Thanks for your comment. Our experimental observations reflect a time-averaged signal resulting from the rapid switching between discrete oxidation states (*e.g.*, 2+ and 1+), rather than a single, stable quantum state with a non-integer charge. We remove the term "fractional charge occupancy" to avoid misleading.

Comment 2-11: Line 263/264: 'The strong electric field interacting with dipole moments results in the energy splitting observed in relaxation process of S02+ and T12+'. The authors did not elude to this before. They even excluded the effect of the electric field. It seems that this statement in the conclusion is thus not well-supported by the claims made in the results.
Reply 2-11: Thanks for your comment. We indeed rule out the electric field effects on the conformation change. However, we notice that the population change is not able to solely interpret our observation of such a huge energy shift and splitting. As we discussed in **Reply 2-1** and **Reply 2-10**, the strong electric field coupling with dipole moment of different excited states in the presence of pump voltage initially induced the energy splitting of S_0^{2+} and T_1^{2+}.
To specify the interaction of pump voltage, we modified in the main text (Page 10 Line 328-330):
"The strong electric field interacting with dipole moments in the presence of pump voltage results in the energy splitting observed in relaxation process of S_0^{2+} and T_1^{2+}."

Some minor criticism:

Comment 2-12: It is not clear if the authors use the word excited state for any state that is not the ground state, e.g. also ground states of other charge states, or only of excited states of a particular charge state.

Reply 2-12: Thanks for your comment. We have revised all descriptions related to excited states. Now, in this manuscript, the term "excited state" is used in a broad sense to denote any non-equilibrium electronic state induced by charge transfer. And for clarity, when referring to specific states, we explicitly use their precise notation S_0^{2+}, T_1^{2+}, etc. to distinguish different charge configurations and excitation processes.

Comment 2-13: The pulse width experiment performed for single pentacene molecules is quite different from the one presented here. The similarity is that a pulse length is swept, but there are many examples of such experiments in literature. I would omit the reference to Jinbo et al. in line 112.

Reply 2-13: Thanks for your comment. We have removed the citation here and relocated it in the Introduction within the section on state-of-the-art electronic pump–probe coupled scanning probe microscopy as well as in the discussion of pulse-induced voltage switching, since it offers a model for voltage-pulse-induced state transitions.

Comment 2-14: Line 159/160, reference 39 is about a different molecule. So this sentence should be omitted or rephrased.

Reply 2-14: Thanks for your comment. Ref. 39 in the context of specific molecular properties may be inappropriate given the difference in the molecular systems. Therefore, we relocated the citation to Line 182 as Ref. 40 (in the discussion of state transition mechanism) since the many-body model employed in our study is derived from this work and it remains a crucial reference for our analysis.

Comment 2-15: The authors write in line 164 that D1+ has a lifetime of 4.7 ns. How do they know?

Reply 2-15: We thank the reviewer for pointing out this omission. We apologize for failing to mention the estimation method for the lifetime in the original manuscript. This value 4.7 ns was derived from the Einstein equation, where the oscillator strength and energy gap were provided by TDDFT. We have revised the text to explicitly clarify this derivation: "the doublet excited state D_1^+ is excluded due to the short lifetime of 4.7 ns estimated by the Einstein equation (see Methods, Computational details)."

Comment 2-16: SI page 11 Fig. S13, in the caption it is written Vg = 0 V for b, but in panel b it is written Vg = -2.5 V. In the same figure, why didn't the authors take the same time region to determine the slope in a and b?

Reply 2-16: Thank you for pointing out this typo error in the caption. We have rectified the inconsistency between the caption and the panel label in **Fig. S10**.

Regarding the time region for slope determination: Our original intention in **Figs. S13a** and **S13b** was to illustrate the derivation of the data points plotted in **Fig. S13c** (now is **Fig. S10**), where each slope corresponds to a specific rate. To address the reviewer's concern and improve clarity, we have updated these two panels. The revised figures explicitly demonstrate the evolution of the slope under pulse width, where the slope exhibits a clear dependence on the pulse width, indicating a time-dependent excitation process in **Fig. S13a** and the slope remains constant no regardless of the pulse

width.

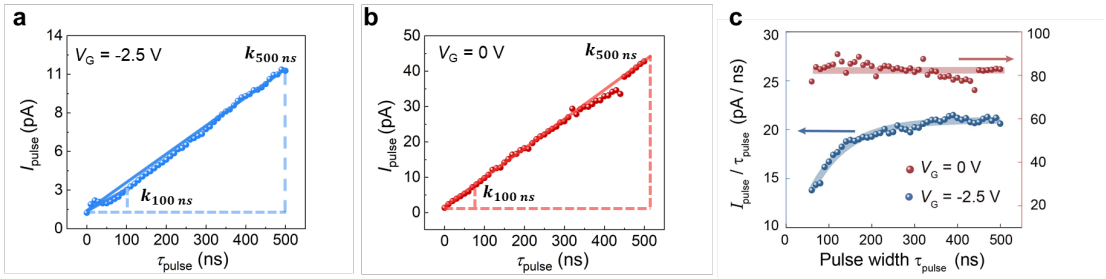


Fig. S10 Single-pulse measurement of the charged single molecule by pulse-width dependence experiment. a,b, Measured pulse current I_{pulse} as a function of pulse width τ_{pulse} with fixed –0.8 V amplitude at V_G= –2.5 V (a) and 0 V (b). c.The normalized pulse current by variable pulse width voltage at V_G = –2.5 V (blue line) and 0 V (red line). The red and blue lines are guides for the eye. The normalization method was to extract the slope of the signal difference under different pulse widths compared to that at τ_{pulse} = 0 ns.

Reviewer #3 (Remarks to the Author):

The paper presents a nanosecond pump-probe study of the excited state dynamics of a single molecule measured by placing the molecule in a transistor device. The main claim of the paper is that this type of experiment allows the authors to access the excited state dynamics of open-shell radicals, which goes beyond what STM-based techniques can achieve. I deem the results to be of high quality and broad interest to the community of researchers studying excited state dynamics at the single molecule level. However, the presentation of the paper needs improving, before it is suitable for publication in Nature Communications. Here is a list of specific points I would like to see addressed by the authors, as well as a few general comments on the presentation.

Comment 3-1: The introduction needs to be expanded on to make it clear why these results are interesting to a broader audience. Moreover, the introduction is a bit confusing as it leaves the reader with the impression that this is an STM study of a device. It is not clear why open shell radicals are inaccessible with STM techniques and how this study goes beyond that.

Reply 3-1: Thank you for this comment. We have summarized two key advances of our study in comparison with conventional STM-based investigations. First, we demonstrate that the electrostatic field generated by a third gate can be used to control the lifetime of excited states. Second, the effective coupling between the electric field and the molecular dipole moment provides an additional degree of freedom for manipulating these excited states. A detailed discussion and the corresponding revisions can be found in **Reply 2-1** to Reviewer 2. We have revised the Introduction to make it accessible to a broader audience as follows:

"The state-of-the-art studies of electronic pump-probe coupled scanning probe microscopy (SPM) offer promising insights into non-equilibrium quantum transport with nanosecond time resolution[17-22]. These techniques provide a powerful platform for probing transient dynamics mediated by electrically induced excited states in single-molecule tunnel junction that are weakly coupled to their environment. However, the orthogonal alignment between electron transport direction and dipole moments of excited states renders the weak electric-dipole interaction, which is essential for electrically controlling the intramolecular interactions of excited states. In single-molecule transistors, the electric field is parallel to the dipole of molecule leading to strong interaction[23-28]. The external gate potential provides an additional electrostatic field to control the charge state and dynamics of single molecule."

Comment 3-2: Figure 1 caption needs to explain everything that is in the figure.

Reply 3-2: Thanks for your comment. To improve clarity for the audience, we have updated a new **Fig. 1** and revised the caption to explicitly detail the distinct roles of the gate, pump, and probe pulses within the single-molecule transistor. The updated caption provides a step-by-step description of the measurement protocol as follows:

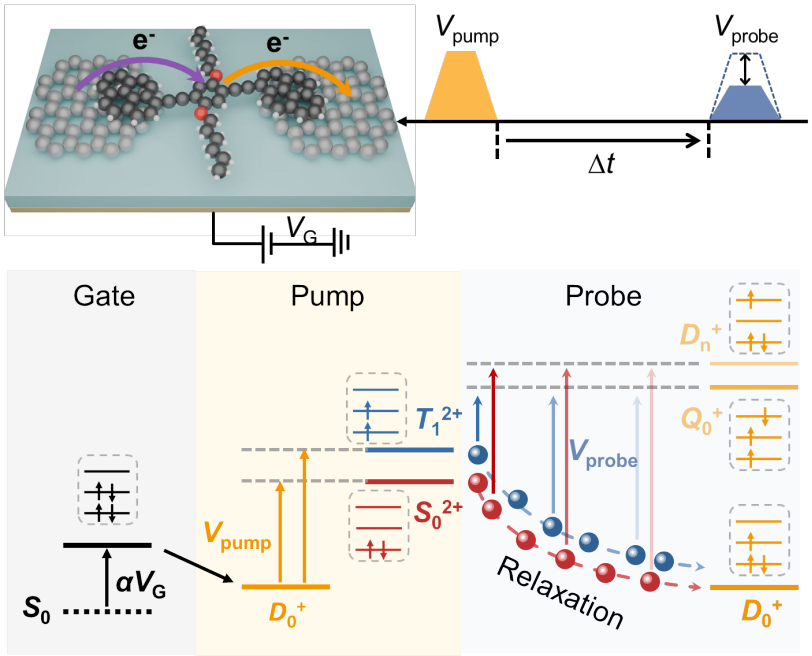


Fig. 1 Schematic of probing the multi-excited states dynamics in the charge transport through a single-molecule transistor using all-electronic pump-probe method. The time delay Δt is defined by the time difference between the falling edge of pump pulse and the rising edge of probe pulse. The process is divided into three stages. Before pumping, the single-molecule junction is initialized to be in a single-electron state by a continuous gate voltage, α is the gate coupling efficiency. During pumping, the co-tunneling mechanism triggers charge and state transitions, resulting in the formation of a series of charged excited states upon the application of a high pump voltage. After pumping, these transient states relax (dissipate) over a timescale of hundreds of nanoseconds. These distinct charge states are detected as resonant peaks in the nanosecond differential conductance spectra, where a transient probe pulse drives the system from the intermediate excited states to higher-lying energy levels. Finally, following the dissipation of the excess charge, the single-molecule radical fully relaxes back to the ground state.

Comment 3-3: It is not clear how it was established that the transistor contains a single molecule. Can you give a concise argument within the main text?

Reply 3-3: Thanks for your comment. The number of molecules incorporated into the circuit directly determines the number of observed Coulomb diamonds. If two molecules are connected in series, forming two molecular quantum dots in sequence, resonant transport can only occur when the energy levels of both molecules lie within the bias window. Because it is highly improbable that the transport levels of two distinct molecules align simultaneously, zero-bias crossing points are generally absent in this configuration. In contrast, when two molecules are connected in parallel, their conductance contributions add up. As a result, transport features from both molecules appear concurrently in the conductance map, making both sets of Coulomb diamonds observable (A detailed discussion to address the number of molecules inside transistor is presented in ***Chem. Soc. Rev.*** 2015, 44, 902).

To clarify this point, we have added a discussion in the main text:

"**Fig. 2b** shows the presence of a Coulomb diamond in a typical stability diagram at 30 K, indicated

by the blue dashed lines. The observation of single resonant transport regime indicating sequential tunneling through single molecular orbital."
A new reference has been added:
Ref. 31: "Chen Z., Woltering S. L., Limburg B., Tsang M. Y., Baugh J., Briggs G. A. D., *et al.* Connections to the electrodes control the transport mechanism in single-molecule transistors. *Angew. Chem. Int. Ed.* **63**, e202401323 (2024)."

Comment 3-4: Line 110 states that the experiment was repeated with another molecule. Can you be more precise about what molecule was used and how it differs from the original molecule? How does this support the claims of the paper?
Reply 3-4: Thanks for your comment. By mentioning that the experiment was repeated with "another molecule", we intended to describe the reproducibility using another single-molecule transistor also based on the **BP** molecule. We emphasize that the key experimental phenomena of pump-probe experiment were consistently reproduced across three independent devices and we concluded them in **Fig. R9** (Details in SI section IV, including the primary data of device 1 presented in the main text in **Fig. 2e** and **Fig. S11**, the replicate data of device 2 shown in **Fig. S12** in the previous version. Additionally, we have added the new data in **Fig. S13** of device 3, where we performed the gate-dependent dynamics measurement of pump-probe experiment. The hundreds of nanosecond relaxation time of devices 2 and 3 is consistent with our primary observation from device 1, suggesting the reliability of our conclusion in dynamics.
As shown in **Fig. R9**, the results from this replicated device are highly consistent with those in **Fig. 2e**, verifying the robustness of our data.

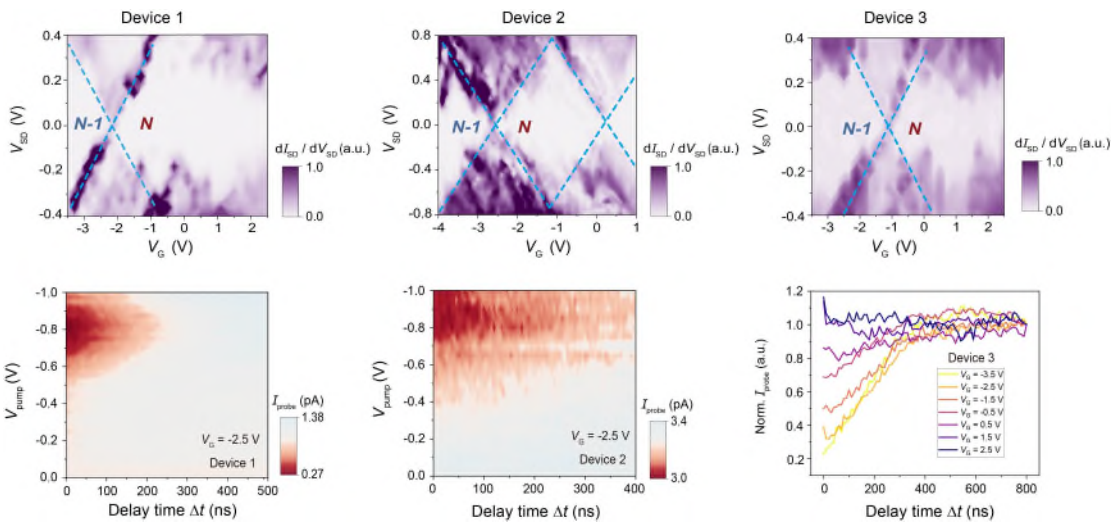


Fig. R9 Pump-probe measurement of three different devices of **BP** molecule.

To clarify this point, we have revised the discussion in the main text (Page 4 Line 134-142):
"The fine feature of pump-probe data is highly sensitive to the molecular orientation and gap size which affects the charge transfer rates, resulting in the incomparability of different devices (see **Section S4**). Despite this, we successfully reproduce the similar phenomenon of this dynamics in device 2 of **BP** (**Fig. S12**), where the transient relaxation dynamics appears with the increase of pump voltage and sustains for hundreds of nanoseconds. Moreover, we realize the control of relaxation dynamics by using gate voltage to control the energy level alignment in device 3 of **BP**

(**Fig. S13**). This demonstrates that gate coupling provides direct electrostatic control of molecular relaxation dynamics, independent of transport bias."

Comment 3-5: Were the spectra in Fig 2 reproducible? Did you repeat the measurements showing the emergence of -0.8 V state?

Reply 3-5: Thanks for your comment. As mentioned in **Reply 3-4**, we have made another **BP** device labeled as device 2 in **Fig. S12**, and repeated the Coulomb stability diagram and pump-probe measurement with similar observation that the transient dynamics become significant when the pump voltage is increasing towards −1 V. The slight difference in energy and dynamics is caused by the fact that it is impossible to build a two completely same device.

Comment 3-6: Fig. 3c &d need more explanations in the caption.

Reply 3-6: Thanks for your comment. We agree that a more detailed explanation of the energy alignment and transport mechanisms is necessary to interpret the schematic. Accordingly, we have expanded the caption for **Figs. 3c** & **3d** to explicitly describe the relevant energy levels, the Fermi level estimation, and the specific orbital contributions to the formation of the charged excited states. The revised caption for **Figs. 3c** & **3d** is:

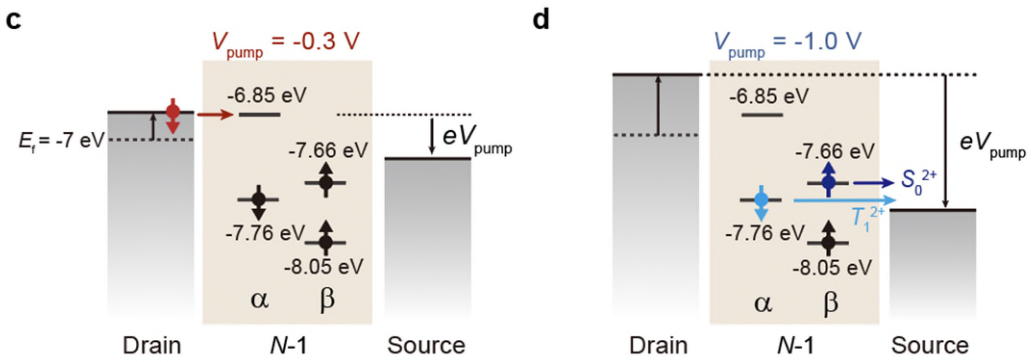


Fig. 3 Single-particle illustration of *N-1→N* (**c**) and *N-1→N-2* (**d**) transition via co-tunneling. The orbital energy levels of the N-1 state relative to the vacuum level are derived from our calculations. Given that the gate voltage is tuned near the N−1/N charge degeneracy point, the Fermi level (E_F) is estimated to be approximately -7 eV, closely aligned with the SUMO orbital (-6.85 eV). Under negative bias conditions in a nearly symmetric junction, the chemical potential of the drain electrode shifts upward while that of the source electrode shifts downward. At low V_{pump}, the drain electrode resonates with the α-SUMO orbital, resulting in electron injection and the formation of S_0 **(c)**. At higher V_{pump}, the source electrode comes into resonance with deeper occupied orbitals, facilitating electron extraction **(d)**. Specifically, the extraction of an electron from the occupied β-orbital leads to the formation of the S_0^{2+} state, while extraction from the occupied α-orbital results in the formation of the T_1^{2+} state.

Comment 3-7: Is the pump-probe data you acquired sensitive to the molecular orientation in the device? Did you perform measurements on more than one molecular device?

Reply 3-7: Thanks for your comment. We agree that the pump-probe data should be sensitive to the molecular orientation which affects the interface coupling strength and resulting the change of tunneling and dephasing rate. While the precise molecular orientation is difficult to control during

the fabrication of single-molecule transistors, we emphasize that the key experimental phenomena of pump-probe experiment were consistently reproduced across three independent devices as mentioned in **Reply 3-4**.

Comment 3-8: The claim on line 246 that this is the first experimental observation of multiple excited state relaxation dynamics needs checking, cf Ferreira, et al Nat Commun, 16, 6039 (2025).
Reply 3-8: Thanks for your comment. We have modified our claim in the main text as follow:
"Our finding provides the direct measurement of multiple excited-state relaxation dynamics induced by electrical stimuli in single-molecule transistor."
In addition, we have added this reference in the main text (Page 6 Line 190-191):
"Although the direct excitation of anion has been observed by light-STM and the energy difference between D_1^+ and D_0^+ states of 0.82 eV is also accessible, the doublet excited state D_1^+ is excluded due to the short lifetime of 4.7 ns."

A new reference cited has been added:
Ref. 43: "Ferreira R. C. C., Sagwal A., Dolezal J., Neuman T., Svec M. Disentangling the components of a multiconfigurational excited state in isolated chromophore with light-scanning-tunneling microscopy. *Nat. Commun.* **16**, 6039 (2025)."

Comment 3-9: Please fix grammar and spelling mistakes across the paper.
Reply 3-9: Thanks for your suggestions. We have carefully rechecked the grammar and spelling of our work, please find the corrections highlighted in the main text and supplementary information.

Overall, I recommend the paper for publication, subject to answering the issues I raise above and improving the presentation.

Point-by-point response to the reviewes' comments

Reviewer #1 (Remarks to the Author):

The authors have addressed all my concerns with new data and refined interpretations; therefore, I recommend the work for publication in Nature Communications.
I have carefully re-read the revised manuscript, the detailed comments from Reviewer 2, and the authors' point-by-point responses. My overall view remains that the experimental work is interesting and that the observation of pump-induced transient spectral features in a gated single-molecule junction is potentially valuable. The revised manuscript has also addressed several of my previous methodological comments. However, after examining Reviewer 2's criticisms in detail, I think that Reviewer 2 is definitely an expert in the field and several core physical questions raised by him/her are indeed substantial and, in my opinion, have not yet been fully resolved by the revised revision. My main concern is not necessarily the experimental observation itself, but rather the strength and specificity of the microscopic interpretations currently attached to it. I believe the manuscript would benefit from a more cautious distinction between what is directly established by the experiment and what remains a plausible, but not uniquely demonstrated, microscopic assignment.
Comments 1-1: The discrepancy between expected charge-transfer rates and extracted lifetimes I agree with Reviewer #2 that the current interpretation tends to associate the observed hundreds-of nanoseconds delay dependence directly with the intrinsic lifetime/evolution of specific doubly oxidized states. There appears to be a quantitative discrepancy here that needs to be addressed. In Reply 2-4, the authors argue for sufficiently strong molecule–electrode coupling in the source–drain junction and, on that basis, for an effective bias lever arm close to unity. At the same time, the measured steady state currents can reach the nA range (Figs. S6 & S7). In such a scenario, it is difficult to reconcile the extremely long apparent lifetimes (hundreds of nanoseconds) assigned to the dication (N-2) states with the expected ultrafast (e.g., picosecond) charge-transfer rates of the junction. It remains plausible that the measured time dependence reflects a more composite nonequilibrium recovery process—such as slower electrostatic/conformational relaxation of the junction environment—rather than the intrinsic lifetime of the proposed (N-2) molecular states. A more quantitative discussion would be helpful. Even a minimal rate-equation or master-equation picture, with reasonable bounds for charge-transfer and relaxation pathways, would substantially strengthen the interpretation and help clarify whether the measured time constants can be consistently associated with the proposed charged states.
Reply 1-1: We thank the reviewer for raising this important point. We agree that the steady-state current in the nA range implies ultrafast charge-transfer processes through the junction. However, we emphasize that the transient signal measured in our pump–probe transport experiment does not directly reflect the intrinsic tunneling time of electrons through the molecule. Instead, it probes the slow recovery dynamics of nonequilibrium transport.
In particular, the change in the transient probe current is at the pA level, corresponding to a small perturbation of the time-averaged steady-state current. This indicates that the measured hundreds-of-nanoseconds time constant is associated with the relaxation of metastable transport states, such as dipole forbidden transition to triplet states (***Nature*** 2002, 419, 278–281), rather than the intrinsic lifetime of the charged molecular state involved in fast charge transfer.

A quantitative rate-equation or master-equation description would require detailed knowledge of multiple microscopic parameters, including asymmetric molecule–electrode coupling, vibrational relaxation pathways, intersystem crossing processes, and electrostatic environment dynamics. These quantities are currently not experimentally accessible in our system, and any minimal model would therefore rely on strongly under constrained assumptions. We therefore refrain from introducing a speculative kinetic model and instead focus on experimentally established trends, such as the strong gate dependence of the transient lifetime (**Fig. S13c,d**), which indicates that the slow dynamics emerge predominantly within specific transport regimes of the N−1 state. The transient features observed in **Fig. 4b** further suggest the emergence of additional states originating from the pump-driven D_0^+ configuration. While alternative mechanisms, such as phonon excitation or conformational changes, may in principle contribute to the observed dynamics, our analysis disfavors these scenarios. Taking together, the experimental observations are consistent with the generation of excited states under electrical excitation.

Comments 1-2: The assignment of Peaks 2 and 3 remains largely qualitative I also find Reviewer #2's concerns on the microscopic state assignment well taken. The interpretation of the transient features still relies heavily on qualitative gas-phase TDDFT level schemes and on an assumed correlation between probe bias and specific many-body transitions. While the proposed picture is certainly suggestive, correlating gas-phase computational energy levels directly to experimental transport resonance voltages is inherently complex and typically subject to significant environmental shifts within the junction. In its current form, the TDDFT calculations provide a qualitative schematic rather than a rigorous quantitative proof of the specific many-body assignments. The evidence therefore appears more consistent with the proposed pathway than uniquely proving it. I would encourage the authors to soften the wording accordingly and avoid overstating the microscopic specificity of the proposed transitions.

Reply 1-2: We thank the Reviewer for this insightful comment and fully agree that the microscopic assignment of Peaks 2 and 3 cannot be considered quantitatively established based on the present calculations. Our TDDFT analysis was intended primarily to provide a qualitative energetic framework illustrating the plausibility of the proposed excitation pathway, rather than a quantitative mapping between gas-phase many-body states and transport resonance voltages in the junction environment. The environmental screening, molecule–electrode hybridization, and electrostatic potential distribution can introduce substantial shifts and renormalizations.

We have therefore revised the manuscript to soften the wording throughout and to explicitly clarify that the TDDFT results serve as a qualitative consistency check supporting the proposed interpretation, rather than constituting definitive microscopic proof of the specific many-body transitions involved.

In particular, we have now stated that the observed transient features are consistent with, rather than uniquely determined by, the proposed excitation pathway.

Comments 1-3: Alternative explanations for the delay-dependent peak motion Reviewer #2's concern regarding the delay-dependent peak shift is also substantial. The revised manuscript discusses global/differential shifts and dipole effects. However, it remains unclear to what extent the observed continuous peak motion can be uniquely attributed to genuine state-energy evolution of the molecule, rather than to population averaging, time-dependent competition between multiple channels, or slower

electrostatic/environmental reorganization of the junction. Since these alternative explanations have not been convincingly excluded, I suggest that this part of the interpretation be presented in a more restrained way, making it clear that the proposed mechanism is a plausible interpretation rather than a uniquely established conclusion.

Reply 1-3: We thank the Reviewer for this thoughtful comment and agree that the delay-dependent peak motion cannot be uniquely attributed to a single microscopic mechanism based on the present data alone. In the revised manuscript, we have therefore clarified that the observed continuous peak shift is interpreted as being consistent with a dynamical evolution of the underlying molecular state energies, while acknowledging that alternative processes may also contribute to the observed behavior. We have revised the discussion in the revised manuscript:

"Given the complexity of the junction environment, multiple factors may potentially influence the observed spectral dynamics. We therefore first assessed whether structural changes induced by charge injection or electric fields could account for the observations through DFT analysis."

"Thus, we propose a physically plausible interpretation summarized in **Fig. 4f**. The overall energy shift may be associated with renormalization effects linked to charge dissipation, as suggested by the observed synchronous evolution of the spectral features. Meanwhile, the time-dependent change in the energy separation between the S_0^{2+} and T_1^{2+} states is consistent with state-specific relaxation dynamics. In particular, the initially observed ~220 meV gap may reflect a differential stabilization of the T_1^{2+} state relative to S_0^{2+}, potentially arising from differences in their effective dipole responses to the local electric field. Such behavior may be more readily observable in single-molecule radical junctions where charge transport occurs along the molecular backbone, which can enhance the coupling between transient charges and molecular orbitals. For comparison, STM-based studies have reported that orthogonal alignment between the electric field and molecular dipole can lead to only microelectronvolt-scale energy shifts[50]. Overall, our results provide experimental indications of complex excited-state relaxation dynamics under electrical excitation in single-molecule transistors, offering a framework for further investigation of nonequilibrium many-body effects in molecular charge transport."

"In summary, we report experimental signatures consistent with the presence of multiple excited states in a single-molecule transistor. The continuous energy evolution in nanosecond scale indicates the strong Coulomb interaction among excited states in single-molecule junctions. The interplay between strong local electric fields and molecular dipole moments under pump bias may contribute to the energy splitting observed during the relaxation dynamics of S_0^{2+} and T_1^{2+} states. These results provide insight into transient charged intermediates that can influence pathways in chemical reactions, photocatalysis, and electrochemical processes, offering a perspective on charge-transfer dynamics at the single-molecule level. More broadly, our approach presents a potential experimental route for probing nonequilibrium states in charge transport through molecular junctions. A comprehensive microscopic understanding of the underlying mechanisms will require further theoretical development and close collaboration with the theoretical community to accurately capture the transient electronic structure of these systems[51, 52]."

Comments 1-4: Clarification of Fig. 3b As a smaller but still relevant point, the meaning of the energy axis in Fig. 3b may benefit from further clarification. The authors state in the rebuttal that the axis refers to "the absolute energy relative to the vacuum level". If so, the figure could be easily misread as showing absolute energetic

separations (e.g., total energy differences or ionization potentials) between different charge states, which typically reside on a different energy scale. It would be helpful to state more explicitly whether Fig. 3b is intended as a quantitative total-energy diagram or as a schematic relative-state alignment.

Reply 1-4: We thank the Reviewer for pointing out the potential ambiguity in the interpretation of the energy axis in **Fig. 3b**. We clarify that **Fig. 3b** is intended as a schematic illustration of the relative alignment of the relevant molecular states, rather than a quantitative total-energy diagram or a depiction of absolute ionization energies. The energy axis is used to indicate the approximate relative ordering of the states with respect to the vacuum level, primarily to guide the discussion of the transport processes. It should therefore not be interpreted as representing precise energetic separations between different charge states.

To avoid possible misunderstanding, we have revised the figure caption and the corresponding text in the manuscript to explicitly state that **Fig. 3b** is a schematic relative-state alignment.

We have also revised the statement in the revised manuscript:

"Based on the TDDFT and experimental results, we proposed the possible schematic energy alignment of both states relative to the Fermi level in **Fig. S16**, which showcases that the orbitals associated with T_1^{2+} are energetically closer to the Fermi level compared to those of S_0^{2+}."

Reviewer #2 (Remarks to the Author):

I want to thank the authors for the effort they put into trying to improve the manuscript. This helped me to further grasp the results and interpretation of the authors. Fig. 2f shows now a spectrum which is similar to the ones obtained in Nat. Nanotechnol. 2025, 20, 27, but in this case with a limited number of signals and less variation in the pulse schemes, and without the ability to assign the peaks based on essentially only the measured spectra (no DFT is necessary in Nat. Nanotechnol. 2025, 20, 27). The further analysis of the experimental data as presented in Fig. 3 and 4 is largely a misinterpretation of the signals, leading to the false claims about states that strongly shift in energy. In addition, the single-molecule junctions are poor to reproduce, which makes it very challenging to derive any quantitative information from these measurements. I, therefore, strongly suggest rejecting this paper.

Reply 2-0: We thank the reviewer for evaluating our revised manuscript. However, we respectfully but strongly disagree with the reviewer's assessment and the recommendation for rejection, as it appears to be based on a fundamental misunderstanding of our dataset and an inaccurate evaluation of our experimental results.

In the previous review round, the reviewer explicitly suggested that we should demonstrate the advantages of applying a gate and source-drain voltage in a single-molecule transistor over scanning-probe microscopy (SPM). We have fully addressed this in last round revision.

1. Regarding the claim of a "limited number of signals", we must clarify our pump-probe measurements contain a more massive and denser dataset compared with previous results in ***Nat. Nanotechnol.*** 2025, 20, 27. As shown in **Fig. R1**, our dynamic evolution curves were measured under a total of 50 different bias conditions (40 curves from 0 V to -1 V with a fine step of 0.025 V, and additional 10 curves with a step of 0.1 V from 0 V to 1 V). Each curve comprises 50 delay time points (from 0 to 500 ns with a 10 ns delay time Δt step). As reported in the **Fig. 4d** in ***Nat. Nanotechnol.*** 2025,

20, 27, transient electronic spectroscopy was performed with a voltage sweep precision of 0.05 V, and only four spectra at discrete delay times were presented. The **Fig. 2f** in our work presents selected few line cuts extracted from the comprehensive datasets in **Fig. 2e** and **Fig. S11a** for visual clarity.

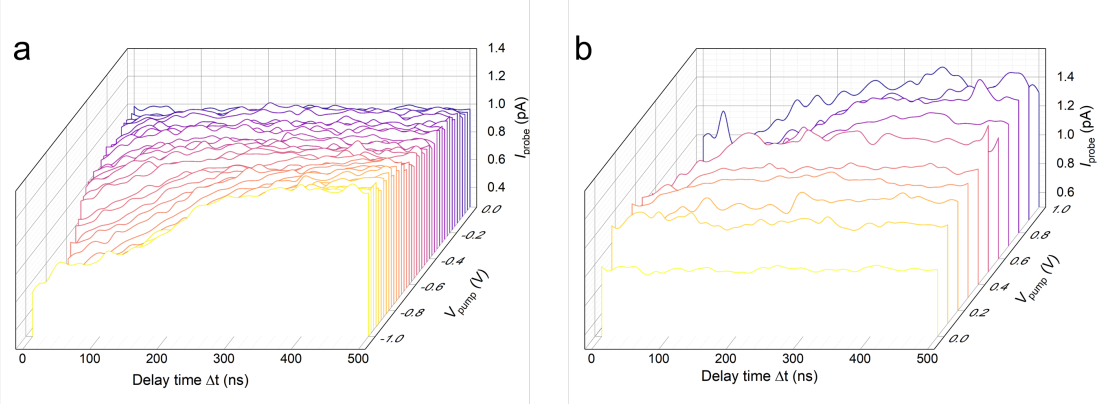


Fig. R1 Pump-voltage-dependent pump–probe dynamics measured under (a) negative bias and (b) positive bias conditions, corresponding to the raw data from **Fig. 2e** and **Fig. S11**.

2. Regarding the claim of "less variation": We agree that the voltage tunable range in our case is relatively narrow compared with that in ***Nat. Nanotechnol.*** 2025, 20, 27, however, our case have already covered the resonant energy of states discussed in our system. In addition, the local heating in single-molecule junction is much stronger than the tunnel junction mode, not suitable for working in high bias voltage regime. As shown in **Fig. R2c**, another work on the transient electronic spectroscopy (***Nat. Commun.*** 2023, 14, 7440, where they studied a two-dimension electron gas system) even only show the variation of voltage in tens of meV range. It makes no sense to increase the voltage variation range when it is already wide enough to uncover the pheonomenon.

[FIGURE REDACTED]

Fig. R2 Transient electronic spectra. (**a**) **Fig. 4d** in *Nat. Nanotechnol.* 2025, 20, 27. (**b**) Our results shown in **Fig. 4b**. (c) **Fig. 2b** in *Nat. Commun.* 2023, 14, 7440.

3. Regarding the claim of "poor reproducibility", the reviewer commented that quantitative information cannot be derived because the lifetimes vary across different devices. However, variations in the extracted lifetimes between different junctions are also commonly reported in previous time-resolved studies based on SPM. Importantly, this does not affect the validity of performing quantitative lifetime analysis on an individual device. We argue that this critique ignores the well-established physical

reality of single-molecule electronics. Device-to-device variation is an inherent characteristic of single-molecule transistors due to the uncertainty of effective configuration and interface coupling. Nevertheless, we observe similar time-resolved trends across three devices supported by observing similar relaxation time, indicating that the main conclusions are **reproducible**. The critical factor is that, within the same device, the observed dynamic phenomena are strictly and reliably reproducible.

Please find below an elaborate discussion of the incorrect statements.

Comments 2-1: The authors compare their data with data presented in Phys. Rev. Lett. 2021, 126, 176801 (Fig. R3). They wrongly state in their rebuttal that in the cited paper the measured data points correspond to the lifetime. Instead, they are the probability that a single electron tunneled during a certain time interval, in other words, they represent a tunneling current. That is why the authors of that paper took a derivative to obtain the energies of the involved states. The authors of the paper under review measure similar curves as presented in Fig. 2f. If they want to reproduce the results from Phys. Rev. Lett., they should then take the derivative of that data, not of the extracted decay rates of the various features observed. In addition, the authors compare their data with Nat. Nanotechnol. 2025, 20, 27 (Fig. R2). Again, they should compare Fig. 2f with this data, and then the authors see that there curves also do not shift in voltage with increasing times, but simply reduce in magnitude.

Reply 2-1: We are fully aware that the data points in the cited ***Phys. Rev. Lett.*** *2021* paper represents the relationship between tunneling current and voltage. However, a thorough review of the subsequent literature clearly reveals that this tunneling current is directly correlated with the charge-state lifetime. Therefore, we kindly direct the reviewer's attention to the follow-up work by same group, titled "Charge-state lifetimes of single molecules on few monolayers of NaCl" (***Nat. Commun.*** 2023, 14, 4988). In this study, the authors demonstrate that the tunneling current can be directly assigned to the charge-state lifetime under saturation conditions. More importantly, they explicitly investigated the relationship between the charge-state lifetime and the applied voltage, concluding unequivocally: “showing that, also independent of the applied bias voltage, the charge-state lifetime remains the same” (Supplementary Information, Page 4, 1st paragraph).

[FIGURE REDACTED]

Fig. R3 Lifetime analysis of (a) the **Fig. 3a** in ***Phys. Rev. Lett.*** 2021, 126, 176801, the (b) **Fig. 3a** and (c) **Fig. S3** in ***Nat. Commun.*** 2023, 14, 4988.

Therefore, our conclusion, that the relationship between the lifetime and voltage manifests as a plateau, is not only physically sound but perfectly consistent with the latest consensus in the field. Our approach introduces an innovative and direct method to measure the charge-state lifetime. We strongly maintain that our data analysis is scientifically rigorous and mathematically robust, and we respectfully request that the reviewer evaluate our direct measurement approach objectively.

Furthermore, regarding the reviewer's suggestion to take the derivative of the raw data (as in **Fig. 2f**) rather than the extracted decay rates, we have also performed this analysis to address the reviewer's concern in **Fig. R4**. We must emphasize that, given the specific nature of our measurement scheme, we do not consider taking the direct derivative of these curves to be a physically appropriate treatment. Nevertheless, it is highly noteworthy that even when applying the reviewer's suggested approach, the resulting derivative data are almost same with the previous analysis used in **Fig. 3a**.
Therefore, we have soften the statement: "Interestingly, the non-quantized correlation between lifetime and pump voltage around V_{pump} = –0.8 V is distinct from the quantized excited state dynamics in an individual naphthalocyanine molecule where the lifetime against the voltage exhibits the plateau-like feature[39]. Such a discrepancy may suggest the involvement of multiple excited states, potentially with coherent interactions, extending beyond a simple picture based solely on charge-state transitions."

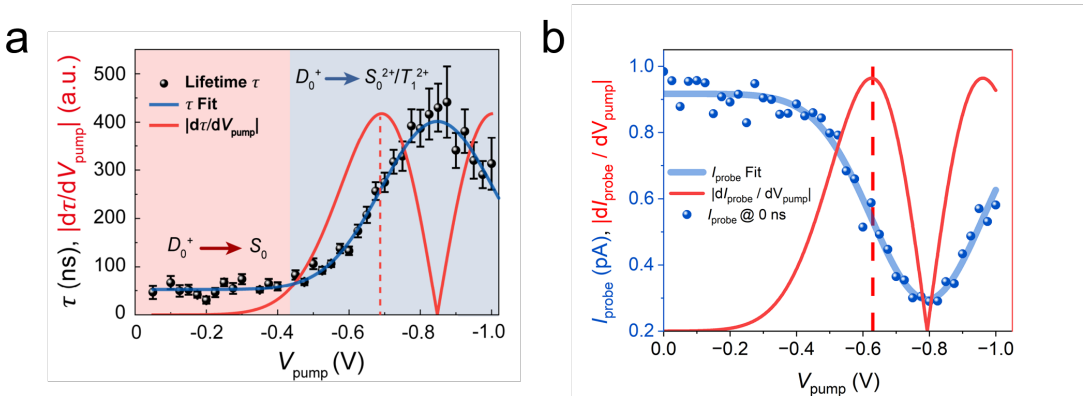


Fig. R4 Derivative of (a, corresponds to **Fig. 3a**) the lifetime and (b) the current.

The reviewer suggests comparing our **Fig. 2f** with the data in ***Nat. Nanotechnol.*** 2025 (**Fig. R2**) and notes that the curves in **Fig. 2f** only reduce in magnitude without shifting in voltage. We cannot accept this conclusion, as it appears to arise from a mix-up between the excitation process and the detection process in our pump-probe measurements. We must clarify that **Fig. 2f** displays our pump (excitation) spectrum, whereas the data discussed in **Fig. R2** pertains to the probe (detection) spectrum. It is a fundamental physical principle in any pump-probe system that an excitation spectrum (**Fig. 2f**) will never exhibit a dynamic energy shift. This is because the resonance energy required to excite a specific state is intrinsically fixed. As expected, its dynamic evolution manifests solely as a decay in intensity (magnitude reduction). The energy shifts we discussed and claimed in our manuscript are observed in the probe (detection) spectrum (**Fig. 4b**), not the pump (excitation) spectrum. Therefore, comparing an excitation spectrum to a detection spectrum to negate our findings is conceptually flawed.

The authors should therefore:

a. Remove the statement: 'Interestingly, the non-quantized correlation between lifetime and pump voltage around Vpump = -0.8 V is distinct from the quantized excited state dynamics in an individual naphthalocyanine molecule where the lifetime against the voltage exhibits the plateau-like feature39. Such a discrepancy suggests the appearance of coherent transition between multiple excited states.'

Reply 2-1-a: We respectfully disagree with the suggestion to remove this statement. The comparison with quantized excited-state dynamics in individual naphthalocyanine molecules is included to highlight the distinct physical regime accessed in our measurements. In particular, the non-quantized correlation between lifetime and pump voltage provides important evidence for the involvement of coherent transitions among multiple excited states. Removing this discussion would weaken the physical interpretation of our observations.

b. Remove the dtau/dV curve from Fig. 3a.

Reply 2-1-b: We respectfully disagree that the dτ/dV curve should be removed. Notably, in the above comment the reviewer even suggested taking a derivative to obtain the energies of the involved states, which is precisely the purpose of this analysis.

c. 'The shift in the branching ratio of transitions into S0 and S02+/ T12+ leads to the observed increase in with pump voltage.' I believe that the observed increase in decay time is because the population of both S02+ and T12+ are increasing.

Reply 2-1-c: We appreciate your comment, however, we believe we are describing the same thing. Furthermore, this statement was made precisely because we accepted your suggestion in the previous review round. As you explicitly commented last time (**Comment 2-5**): "it seems that the signal being measured is a time-average over a single molecule, which could explain the increase in tau with pump voltage by altering the ratio of tunneling into S0 vs S02+/T12+". A shift in the branching ratio naturally means an increase in the population.

d. 'This closer proximity implies a higher tunneling probability for T1, which accounts for Gaussian shaped Iprobe regime around Vpump = 0.8 V in Fig. 2f.'

Reply 2-1d: We respectfully appreciate your comment.

i. The authors do not explain why at negative and positive gate voltages S02+/T12+ are accessed? In AFM experiments at negative and positive gate voltages different charge states will be accessed. It would be helpful if the authors draw the full many body diagram at different gate voltages to explain this, as well as illustrate this in single-particle pictures. The fact that it is accessed at both positive and negative gate voltages could be explained by the drain and the source being present. However, this is in contrast to figure 4d, where it is indicated that at positive gate voltages S02+/T12+ are emptied, not occupied.

Reply 2-1-i: Thanks for your comment. However, we must point out a fundamental misunderstanding: the V_{pump} discussed here is applied to the source-drain voltage, not the gate voltage. Furthermore, as for your request to "draw the full many-body diagram at different gate voltages... as well as illustrate this in single-particle pictures", our **Figs. 3b-d** already explicitly present the many-body diagram and the single-particle pictures, respectively.

To improve the readability of how the excitation occurs, we have provided an additional demonstration using the Coulomb diamond of a single-electron transistor as an example in **Fig. R5**. In our case, the constant gate voltage is applied such that the operating point

is positioned slightly to the left of the degeneracy point between the 0 and -1 charge states. Starting from this specific gate position, applying a small source-drain bias voltage (pump pulse) will open a transport window that induces the (-1,0) states, which corresponds to a single electron tunneling out. As the applied bias voltage (pump pulse) is further increased, the bias window expands to encompass the next energy level, thereby inducing (-2,-1,0) states. Therefore, it is a well-established physical fact in such setups that the exact same charge/excited states can be accessed and excited under both positive and negative source-drain bias voltages.

[FIGURE REDACTED]

Fig. R5 A general stability diagram showing Coulomb diamonds of a single-molecule transistor. Reproduced from **Fig. 2a** in ***Mater. Quantum. Technol.*** 2023, 3, 025003.

ii. In addition, the Gaussian-shapes are explained in STM/AFM experiments by the phonon-induced broadening because of the underlying NaCl surface. In the manuscript under review the signals at positive and negative gate voltage are similarly broadened, the authors should explain what the origin of this broadening is.

Reply 2-1-ii: Thanks for your comment. In our case, the observed broadening originates from the coupling between the molecule and the electrodes, which leads to phonon-induced broadening of the electronic states.

To clarify this point, we have added a description of the origin of the broadening in the revised manuscript: "The observed broadening originates from the coupling between the molecule and the electrodes, leading to phonon-induced broadening of the electronic states."

iii. The reduction of the signal at -1 V in 2f and 3a could be explained by opening an additional decay channel at higher applied gate voltages. The authors do not consider such decay pathways during the applied probe pulse.

Reply 2-1-iii: This comment is exactly consistent with what we have already described in the manuscript. As we explicitly considered the T_1^{2+} state as this additional decay channel. In our manuscript (Line 202 to 204), we wrote: "At V_{pump} around −0.6 V, the S_0^{2+} state gradually increases to be the dominant state, resulting from the removal of one electron from SOMO. As V_{pump} < −0.8 V, reaching the energy level of highest occupied molecular orbital−1 (HOMO-1), the T_1^{2+} state replaces S_0^{2+} to be the dominant state."

We have revised the statement in the revised manuscript:

"The two peaks of dτ/dV indicates the appearance of new decay channel at V_{pump}=-1V."

Comments 2-2: Related to Fig. 4a:
a. The negative signal is nicely explained by re-excitation of D0+ to doubly charged states. Because of the broadening of the peak, I would explain the fact that the signal appears earlier at -1 V then at -0.7 V by the fact that the tunneling rate is faster at higher applied voltages. This is also in line with the abovementioned potential faster decay of S02+ and T12+ at -1 V. It is also hard from plot b to see the signal between 0 and 100 ns delay time.
Reply 2-2a: We thank the reviewer for appreciating our assignment of the negative signal (peak 2). However, we would like to clarify two important points regarding the interpretation. Firstly, the signal presented in **Fig. 4b** corresponds to the differential conductance rather than the tunneling current itself. An example is that even the high voltage regime showing high current or tunneling rate, differential conductance is always a sufficient tool to extract the information of states locating in the high voltage regime like every one did in the SPM community. Therefore, our analysis is based on the position and evolution of the resonance features, rather than directly on the tunneling rate. Moreover, the **Figs. 4a, b** were measured by probing the change after the pump pulse disappear. All of the energy resonance features are from nonequilibrium states. The differential conductance indicates the energy of those states at different delay time. The delay time is not an indication of lifetime.
Secondly, we respectfully disagree with the interpretation that "the signal appears earlier at −1 V than at −0.7 V due to a faster tunneling rate at higher applied voltages". As shown in previous work (***Nat. Commun.*** 2023, 14, 4988), once the excitation energy exceeds the tunneling barrier, the tunneling rate (lifetime of charged state) no longer increases significantly with increasing bias. Therefore, the earlier appearance of the signal at −1 V cannot be attributed to a higher tunneling rate. Regarding the visibility of the signal between 0 and 100 ns in **Fig. 4b**, we acknowledge that it is not clearly resolved and have improved the presentation in the revised manuscript to make this feature more evident.

b. In case of peak 2 and 3: I would explain the shift of the signal in that case to a difference in tunneling rate if you are well above the resonance peak or if you are at a tail, where the tunneling rate is lower. In other words, at short delay times you can only tunnel well above the resonance peak, while you need longer delay times to also be able to tunnel at the tail.
Reply 2-2b: Thanks for your comment. The assignment of peaks 2 and 3 is based on the evolution of the resonance features as a function of delay time in **Fig. 4b**. Importantly, this measurement does not provide direct information on the tunneling rate; instead, it reflects the differential conductance and the position of the resonant states at different delay times.
In contrast, the tunneling rate is more directly related to the absolute current, which depends on the integrated transmission probability over the relevant energy window. Differential conductance (*dI/dV*), however, is sensitive to the energy derivative of the current and therefore primarily reflects the alignment and evolution of resonant states rather than the absolute magnitude of the tunneling rate. As a result, changes in tunneling rate alone would mainly affect the signal amplitude, whereas the observed continuous peak shift corresponds to a change in the resonance condition in energy.
While variations in tunneling rate, such as those arising from accessing the tail versus the center of a resonance, may in principle influence the signal, they are not expected to produce the systematic energy shift observed here. We have therefore interpreted the

delay-dependent peak motion primarily in terms of evolving resonance positions, while acknowledging that additional effects may contribute.

c. This is related to the presentation in Fig. 1: Probe phase seems to imply that the energies of S02+ and T12+ reduce till they are at the level of D0+, however, I believe the energies stay the same, but the way the signal is being probed it appears to be a shift.
Reply 2-2c: We appreciate your comment. To avoid misunderstanding and improve the readability to a broad audience, we remove the indication of energy shift in **Fig. 1**.

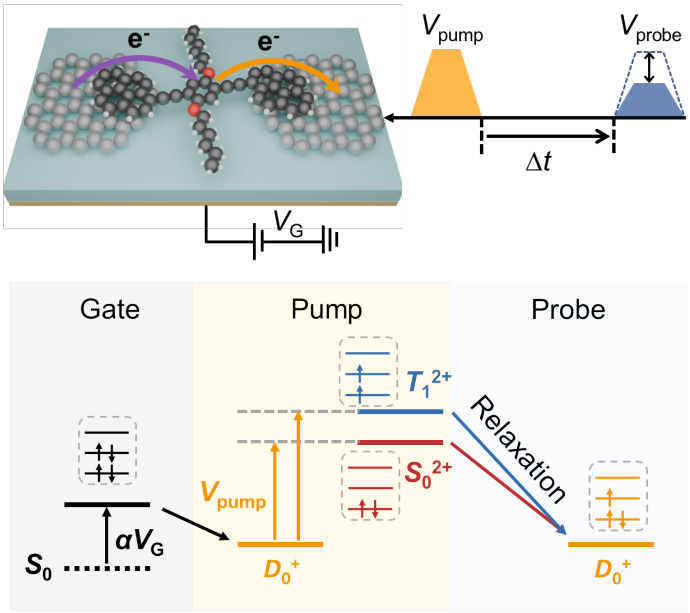


Fig. 1 Schematic of probing the multi-excited states dynamics in the charge transport through a single-molecule transistor using all-electronic pump-probe method.

3. The authors already indicate that: 'The fine feature of pump-probe data is highly sensitive to the molecular orientation and gap size which affects the charge transfer rates, resulting in the incomparability of different devices'. They also state in the caption of Fig. S12 that the 'dynamic behavior of Device 2 shown in Fig. S12b was 221 essentially consistent with the phenomena previously observed'. They hardly show any data for Device 2, which makes it hard to compare. The limited data already hints at a slightly different lifetime. In other words, the authors need to tone down drastically their claims about lifetimes, they measure always decay times which are highly sensitive to the exact fabrication of their device.
Reply 2-3: Thanks for your comment. Variations in the extracted lifetimes between different junctions are also commonly reported in previous time-resolved studies based on SPM (***Science*** 2021, 373, 452, ***Nat. Nanotechnol.*** 2025, 20, 27). However, this absolute variance between devices does not compromise the validity of the dynamics extracted from a single device. The critical requirement for reliable quantitative analysis is intra-device reproducibility. As we have explicitly demonstrated in **Fig. S10**, the dynamic curves and the extracted lifetimes are highly reproducible across multiple sequential measurements within the same device.

Other comments:

Comment 2-4: Fig. 2c: Is Vpulse the same as Vpump later on? The authors describe their pump-probe pulse sequence and then it is confusing that they suddenly introduce

a pulse in general. In my understanding that is the same as Vpump, and the authors should rename it.

Reply 2-4: Thank you for your comment. Yes, the waveform of V_{pulse} is exactly the same as V_{pump}. The reason we initially used V_{pulse} was to first detect the device's response to a single pulse (i.e., applying V_{pump} without V_{probe}). We have now changed V_{pulse} to V_{pump} in the revised manuscript and figures as requested.

Comment 2-5: In Fig. 2e, the authors show data for a pump pulse with a delay time, there is no probe pulse mentioned, what does the delay time then represent?

Reply 2-5: The presence of the probe pulse and the definition of the delay time are explicitly indicated in multiple places in the manuscript. Specifically, the caption of **Fig. 2e**, the Methods section, and the inset schematic of the figure all clearly show that the measurement follows a pump–probe configuration, where the probe pulse is used to read out the current after excitation by the pump pulse. Again, **Fig. 2e** presents the probe current as a function of the pump voltage and the delay time between the pump and probe pulses. The delay time refers to the temporal separation between these two pulses. Given that this information is already clearly provided, the statement that no probe pulse is mentioned appears to arise from a misunderstanding.

Comment 2-6: 'We attribute this difference to the negative bias exciting a discrete state (corresponding to the sharp peak at -0.65 V in Fig. 2c) with a low dephasing rate, whereas the positive bias excites a continuum state (corresponding to the broad shoulder at 0.5–1.0 V in Fig. 2c) exhibiting a much higher dephasing rate.' Comparing Fig. 2c up and down panel it is not apparent at all that the peak is sharp at -0.65 V and continuum at 0.5-1.0 V. There is also a background signal at top panel. As far as I understand the authors could just omit the statements about discrete and continuum and only focus on the dephasing rates? If they want to make this point they should show clear data that these peaks are sharp versus continuum.

Reply 2-6: Thanks for your comment. we have removed the description in terms of discrete and continuum states, as well as the wording related to "sharp" features. In the revised manuscript, we instead focus on the experimentally supported differences in dephasing rates.

Comment 2-7: In the caption of figure 2: 'The inset illustrates that the D0+ can be set to a virtual state (dashed line) with high energy' The energy of D0+ is raised by the applied voltage, it is not a virtual state, please rephrase (the authors show this also correctly in another figure).

Reply 2-7: We thank the reviewer for this suggestion. The term "virtual state" is not appropriate in this context. Therefore, we have removed this wording and revised the sentence to: "D_0^+ can be set to a high-energy state."

Comment 2-8: I assume Fig. 3a is derived from fitting the data in Fig. 2e, the authors should explain this better. Why do they only show the data for negative gate voltages and not also for positive gate voltages?

Reply 2-8: We thank the reviewer for this suggestion. **Fig. 3a** is indeed derived from fitting the data shown in **Fig. 2e**, and we have now clarified this point in the revised manuscript.

Regarding the absence of data at positive pump voltages, our junction can be considered approximately symmetric, and the dynamical behavior under positive and negative bias

is qualitatively similar. Therefore, for clarity of presentation, we showed only the fitted lifetimes at negative gate voltages. Following your comment, we have now present the corresponding lifetime data at with both negative and positive pump voltages in the **Fig. R6**.

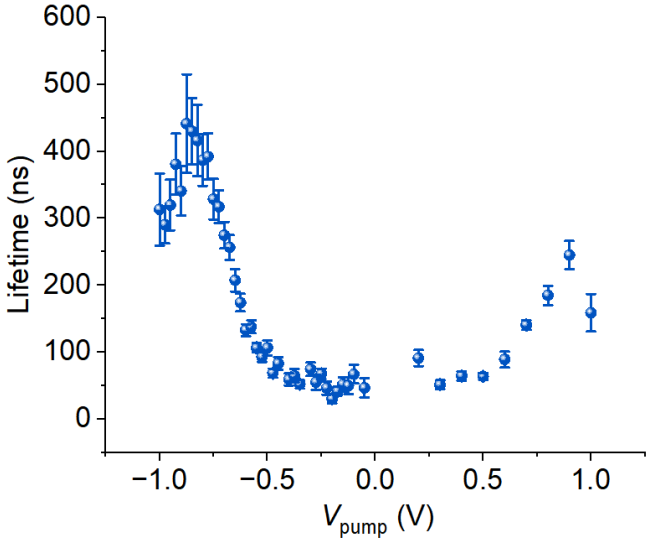


Fig. R6 Corresponding lifetime data with both negative and positive pump voltages.

Comment 2-9: 'Since differential conductance is proportional to the density of state, the value of Gtransient presented in Fig. S22 could indicate the population of electrically stimulated transient species' That would mean that the density of states is the same for every of the states, and the tunneling barriers are the same. This can essentially be ruled out because there are different orbitals involved with different tunneling barriers and different coupling to the leads.

Reply 2-9: Thanks for your comment. We would like to clarify that we do not intend to directly compare the differential conductance between different states. Instead, our interpretation is restricted to a given state, for which the differential conductance is proportional to its local density of states and can therefore reflect its population. Accordingly, we have revised the statement as follows:

"Since the differential conductance associated with a given state is proportional to its density of states, the value of $G_{transient}$ presented in **Fig. S22** can be used as an indicator of the population of electrically stimulated transient species."

Comment 2-10: Related to Fig. S13: What is the relation between panel b and d? If the lifetime is extracted from the data in panel b, then it seems the lifetime/decay time is similar for the whole range of gate voltages between 0.5 V and 2.5 V. Fig. S13c is also not helpful at all to try to explain a difference in lifetime. If there is a real effect here, I believe it is again due to the broadening of the states.

Reply 2-10: We thank the reviewer for the questions. The lifetime in **Fig. S13d** is extracted from the dynamic curves shown in **Fig. S13b**. We note that no lifetime values are reported in the gate-voltage range between 0.5 V and 2.5 V because the dynamical signal cannot be observed in this regime. In this range, the molecule is predominantly in the N charge state, and the population of the $N-1$ state is therefore very low, preventing the pump pulse from efficiently triggering the corresponding dynamics. Under the condition of a fixed V_{pump}, sweeping the gate voltage V_{gate} directly tunes the

energy difference between the two different charge states. **Fig. S13c** is specifically designed to explain this phenomenon.
Regarding your hypothesis that the lifetime variations are due to the "broadening of the states", we agree with this since it perfectly aligns with our explanation. As shown in **Fig. S13d**, the lifetime initially exhibits an upward trend (between -0.5 V to -2 V) because of the energy broadening of the state involved. However, once the excitation energy provided by exceeds the energy broadening of the excited state, the lifetime reaches a plateau and remains almost entirely unchanged (between -2.5 V to -3.5 V).
To solve above concerns, we have revised the caption of this figure.

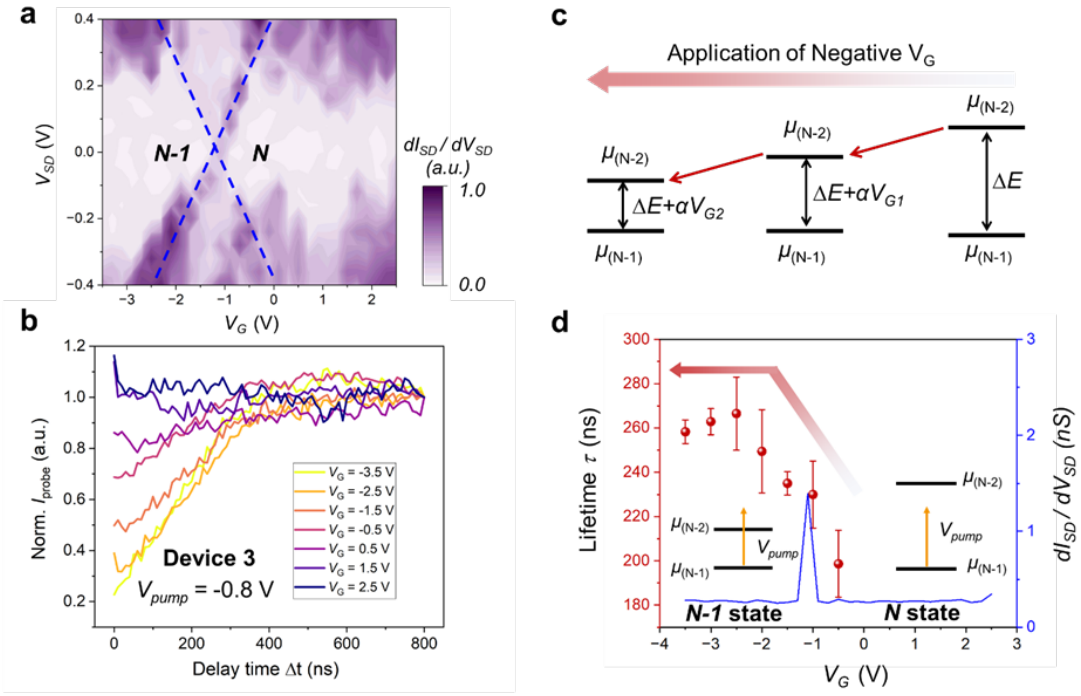


Fig. S13 All-electronic pump-probe measurements of the BP molecule in device 3. **a.** Charge stability diagram of device 3 showing the differential conductance (dI_{SD}/dV_{SD}) as a function of bias voltage (V_{SD}) and gate voltage (V_G) at 30 K. **b**, Corresponding dependence of the probe current I_{probe} on the delay time as a function of gate voltage $V_{gate.}$ at a fixed pump voltage V_{pump} = –0.8 V. **c**, Many-body energy diagram illustrating gate-induced modulation, in which the energy gap between the $N-1$ and $N-2$ states decrease as a negative gate voltage V_G applied. **d**, Differential conductance (dI_{SD}/dV_{SD}) at V_{SD} = 0 V (blue line) and the lifetime of electrically excited states (red dots) as a function of continuous gate voltage V_G. The lifetime is extracted from the dynamics curves in Fig. S13b. The peak around $V_G \approx -1$ V in the differential conductance indicates the transition from the N state to the $N-1$ state. Under the condition of a fixed V_{pump}, sweeping the gate voltage V_G directly tunes the energy difference between the two different charge states. Correspondingly, the transient dynamics become pronounced at $V_G < -1$ V, since the population of the $N-1$ state is negligible for $V_G > -1$V. The lifetime initially exhibits an upward trend (between −0.5 V to −2 V) because of the energy broadening of the involved state. However, once the excitation energy provided by exceeds the energy broadening of the excited state, the lifetime reaches a plateau and remains almost entirely unchanged (between −2.5 V to −4 V).

Comment 2-11: In STM configurations you can also have molecules with an out-of-

plane dipole, e.g. if the molecule is not flat. The authors should add the word typically in their new sentence: However, the typically orthogonal alignment between electron transport direction and dipole moments of excited states renders the weak electric-dipole interaction.
Reply 2-11: Thanks for your kind suggestion. We have revised our statement.

Comment 2-12: The authors should check the English in the paper; there are many mistakes leading to many sentences that cannot be easily read.
Reply 2-12: Thanks for your kind suggestion. We have checked the grammar thoroughly.

Reviewer #3 (Remarks to the Author):
I am satisfied that the changes made by the authors resolved the issues that I raised previously and I recommend the paper for publication in Nature Communications.
In a confidential comment to the editors, Reviewer #3 also agrees that Reviewer #2's points should be adequately addressed before publication. In particular, Reviewer #3 notes that "the main point that I consider harder to rebut is the reproducibility of the data across the two molecules. However, the method used by the authors is much more accessible than UHV SPM, and therefore if they could provide more data obtained using device 2, it would significantly strengthen the paper."
Reply 3: We sincerely thank the Reviewer for the careful evaluation of our manuscript and for the constructive comments provided throughout the review process. We are pleased that the revisions have satisfactorily addressed the concerns, and we greatly appreciate the Reviewer's recommendation for publication.
For the additional comment raised by reading the reply of Review #2, since Device 2 corresponds to our initial experimental realization, in which the key dynamical behavior was first observed. In fact, as also shown in **Fig. S13**, a Device 3 further provided consistent observations, including gate-dependent modulation of the dynamics and the associated lifetimes. These results corroborate the generality and reproducibility of our findings beyond a single device. Please also refer to **Reply 2-0**, we have also made a demonstration about the reproducibility of single-molecule transistor.

Reviewer 1:

I have carefully read the revised manuscript and the authors' responses to the referees. I agree with Reviewer #2 that the precise microscopic assignments, including the origin of the apparent nanosecond energy drift and its relation to specific many-body states, remain somewhat interpretative and are not uniquely established by the current data. However, I note that the authors have made reasonable efforts to soften their claims and present their interpretation in a more cautious manner. In my view, the main contribution of this work lies in the experimental methodology and the observation of non-equilibrium charge dynamics in a single-molecule device, which is novel and valuable. Therefore, I maintain my recommendation that the manuscript can be accepted for publication in Nature Communications.

Reply 1: Thank you for the recognition of our experimental methodology's novelty and continued feedback. We agree with your comment—aligning with Reviewer #2—that the precise microscopic origin of the apparent nanosecond energy drift remains interpretive. To address this shared concern, we have further revised the discussion regarding Fig. 4 in the manuscript, as detailed in our response to Reviewer #2.

Reviewer 2:

I thank the reviewers for answering my questions and concerns and clarifying and resolving most of them. In a few cases, I misunderstood the author’s statements, and I want to thank them for clarifying them in their rebuttal. There is one remaining issue where we have not reached a consensus yet, after resolving that issue, I am fine if the manuscript is published.

Reply 2-1: We sincerely thank the reviewer for the careful re-evaluation of our manuscript and for the positive assessment of this manuscript being considered suitable for publication. We greatly appreciate the reviewer’s constructive comments, which have helped us to further clarify the interpretation of Fig. 4 and avoid overstating the experimental conclusion.

Following the reviewer’s concern, we have revised the relevant text throughout the manuscript. In particular, we no longer state that the excited states definitively “shift in energy” during the delay time. Instead, we now describe the experimental observation as a time-dependent evolution of transient conductance features, and we present the Coulomb renormalization and state-specific relaxation as physically plausible interpretations rather than definitive assignments. These changes are intended to make the conclusion more cautious and more consistent with the experimental evidence.

My issue is related with Fig. 4, and its interpretation. I still cannot believe that the states are actually shifting in energy during the delay time, and the authors do not provide sufficient proof for these statements, and do not clearly exclude other effects. Already in accordance to the feedback of reviewer 1 the authors slightly toned down their statements, but the authors still clearly claim that the states shift in energy. The authors write in their rebuttal: ‘we respectfully disagree with the interpretation that “the signal appears earlier at -1 V than at -0.7 V due to a faster tunneling rate at higher applied voltages”. As shown in previous work (Nat. Commun. 2023, 14, 4988), once the excitation energy exceeds the tunneling barrier, the tunneling rate (lifetime of charged state) no longer increases significantly with increasing bias. Therefore, the earlier appearance of the signal at -1 V cannot be attributed to a higher tunneling rate.’ The

authors incorrectly compare to this paper, where special measurement conditions are employed under saturation conditions. Under such saturation conditions the signal is independent of the bias voltage. The observation of non-step like features in Fig. 1f indicates that the authors do not work under these conditions, and therefore, they should compare with the results from Phys. Rev. Lett. 2021 and Nat. Nanotechnol. 2025, as they also did at other places in the manuscript. There it is clearly visible that the signal still increases till a plateau is reached.

Reply 2-2: We thank the reviewer for pointing out the limitation of our previous comparison. We agree that the cited work used a different experimental technique and was performed under different measurement conditions; therefore, a direct quantitative comparison with our all-electronic pump–probe spectroscopy in a single-molecule transistor is not appropriate. We have revised our response accordingly and no longer use this comparison as direct evidence to exclude voltage-dependent tunneling-rate effects.

Nevertheless, we would like to clarify the motivation behind our discussion. The non-step-like dependence of the extracted lifetime on pump voltage indicates that the dynamics in our junction cannot be fully described by a simple charge-state redox process alone. This behavior differs from the saturation-like voltage-dependent lifetime reported in previous studies, where the dynamics were dominated by a single charge-state transition under different measurement conditions. In addition, recent time-resolved excited-state spectroscopy of individual molecules has shown that multiple transient states can exhibit distinct decay dynamics. Although the lifetimes of each individual state were not separately quantified in that work, the observation supports the general idea that the involvement of multiple transient states can lead to more complex voltage-dependent relaxation behavior.

We would also like to emphasize that our analysis is not simply based on the fact that the signal appears earlier at −1 V than at −0.7 V. In our measurements, the lifetime is directly extracted from the delay-time dependence of the pump–probe response, as summarized in Fig. 3a. This provides direct temporal information on the nonequilibrium relaxation dynamics. In addition, the transient I_{probe}-V_{probe} data are converted into nanosecond-resolved differential-conductance spectra, which provide an energy-resolved readout of the transient conductance features. This distinguishes our approach from measurements that monitor only time-domain current responses. The differential-conductance analysis enables us to separate multiple transient features with relatively small energy separations and to compare their temporal evolution.

We have revised the manuscript to make this distinction clearer. Specifically, we now describe Fig. 4 as showing a delay-time-dependent evolution of transient differential-conductance peak positions, rather than direct proof of intrinsic excited-state energy shifts. We also explicitly acknowledge that voltage-dependent tunneling rates may contribute to the observed dynamics. Nevertheless, the simultaneous observation of distinguishable transient peaks, their different decay behaviors, and their correlated spectral evolution suggest that multiple excited-state-related pathways are involved. Coulomb renormalization and state-specific relaxation are therefore presented as possible physical interpretations consistent with the data, rather than as conclusive assignments.

I believe that the results in Fig. 4a are similar as in those papers, and therefore that the results in Fig. 4b cannot be interpreted as a shift of the energies of the states. The authors later on even acknowledge: ‘While variations in tunneling rate, such as those arising from accessing the tail versus the center of a resonance, may in principle influence the

signal', but then state that 'they are not expected to produce the systematic energy shift observed here.' The argumentation why that is not the case they provided earlier, and there I disagree with. I strongly suggest removing this interpretation of a shift of the state energy in Fig. 4 and the corresponding description and instead propose several reasons for the observed data in Fig. 4b, including the statement they already have about the averaging, as well as a statement about the influence of the broadening of the peaks.

Reply 2-3: We sincerely thank you for your continued feedback, and for helping us reach a consensus on this final point. We appreciate your critical and rigorous assessment regarding the interpretation of Fig. 4. Given the complex non-equilibrium conditions, referencing the apparent peak evolution merely as a direct eigenstate energy shift could indeed be misleading and overlooks the influence of tunneling rates and energy broadening.

Following your recommendation, we have removed the definitive claims of a direct energy shift of the molecular states throughout the manuscript (including the abstract and discussion). Instead, we have extensively revised the discussion of Fig. 4 to present a more cautious, comprehensive, and physically rigorous interpretation. Specifically, in the revised manuscript, we now explicitly state that the observed peak position reflects the possible contributions from Coulomb renormalization and local charge redistribution, rather than the energy of molecular state.

The revised abstract as follows:

"Here, we resolved the dynamics of multiple excited states during non-equilibrium charge transport through a single-molecule radical junction using a nanosecond differential conductance spectroscopy. The participation of singlet and triplet states is revealed in both time and energy domains occurring within ~150 ns mediated by doublet states. In addition, the transient resonance positions evolve by up to ~440 meV over hundreds of nanoseconds, consistent with a dynamic realignment at the molecule–electrode interface during charge dissipation. We interpret this behavior as a signature of Coulomb-renormalized transport resonances rather than as direct evidence for isolated molecular eigenstates shifting in energy."

In the main text discussing Fig. 4, we have incorporated the alternative explanations proposed by the reviewer. We have explicitly expanded our discussion as follows and highlighted in the revised manuscript:

"To elucidate the role of excited states during discharging dynamics with following resonant excitation, we acquire probe-voltage-dependent dynamics with the pump voltage fixed at –0.8 V as presented in Fig. 4a (Details in Methods, Transient *I-V* measurement). A time-dependent Coulomb blockade region emerges over a 0–500 ns timeframe, with features distinct from those observed in the pump-voltage-dependent dynamics. The apparent motion of the conductance boundary with delay time indicates a time-dependent change in the transport resonance condition. We do not interpret this observation as direct proof that isolated molecular eigenstates rigidly shift in energy. Rather, the data reflect the delay-dependent alignment between molecular many-body states and the electrode chemical potentials, which can be influenced by Coulomb renormalization, charge redistribution, local electric fields and state-dependent tunneling rates. Importantly, a blank graphene tunnel junctions without molecules show no comparable response to either pump or probe voltage pulses, indicating that the observed dynamics originate from the molecular junction rather than from trap states in graphene[46]."

"The electronic pump-probe technique can, in principle, average discrete quantum transition events into smoothed I_{probe}-V_{probe} responses through repetitive excitation cycles. However, the observed dynamics suggest a more complex origin. We extract the peak energies of them at every delay time presented in Fig. 4e. Peak 1 (D_0^+) and Peak 3 (S_0^{2+}) evolve in a correlated manner, suggesting that part of the spectral motion reflects a global change in the electrostatic alignment of the molecular junction during charge relaxation. However, these apparent resonance shifts should not be interpreted as direct measurements of rigid molecular-state energy shifts. In a pulsed transport experiment, the observed peak position reflects the voltage required to satisfy a transient tunneling condition and can therefore be affected by state population, tunneling rate, local electrostatic potential, charge redistribution and Coulomb renormalization[47]. Within this framework, Peaks 2 (T_1^{2+}) and 3 (S_0^{2+}) show different delay-dependent resonance trajectories, with apparent shifts of ~440 meV and ~220 meV within ~150 ns, respectively.

Given the complexity of the junction environment, multiple factors may potentially influence the observed spectral dynamics. We therefore first assess whether structural changes induced by charge injection or electric fields could account for the observations through DFT analysis (Supplementary Figure 19). The calculated results show that geometric modifications lead to only minor orbital-energy perturbations (<0.1 eV; Supplementary Figure 19), which are much smaller than the apparent resonance-position changes observed experimentally. We therefore consider structural relaxation unlikely to be the dominant origin of the transient spectral evolution.

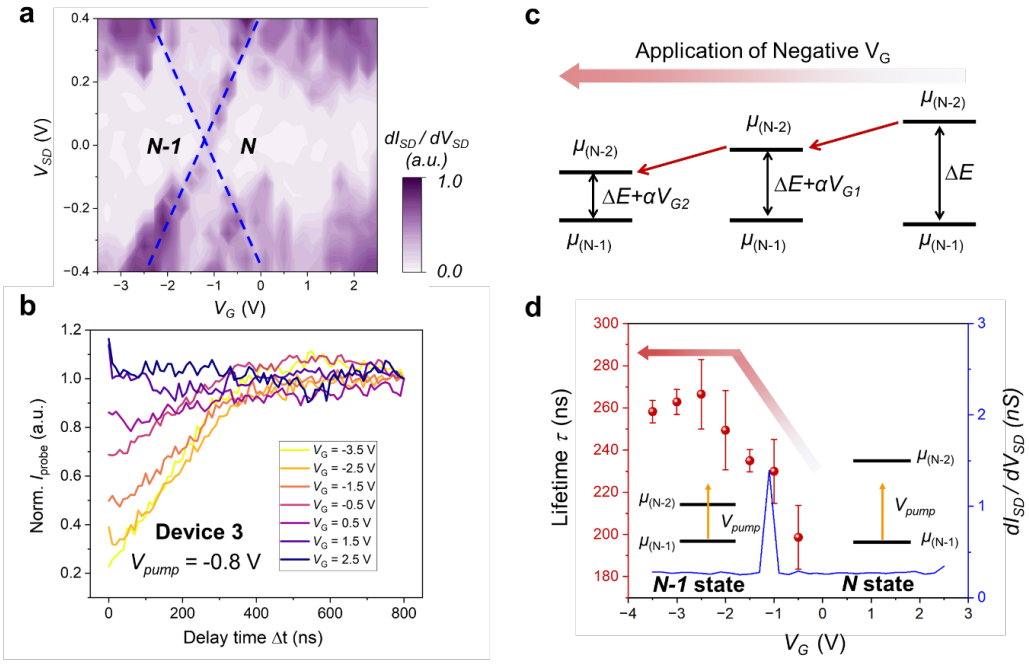
The strong external electric field in single-molecule junction (~10^8 V/m) during the pump pulse could, in principle, alter the transient transport resonance conditions through coupling to molecular dipoles and local charge redistribution[24, 48, 49]. The calculated dipole moment (Supplementary Table 2) suggests that the coupling strength of D_0^+ and S_0^{2+} are nearly the same, whereas that of T_1^{2+} is significantly smaller. This difference may contribute to the distinct initial resonance positions of Peaks 2 and 3, although we do not assign the observed resonance evolution solely to a Stark shift of molecular eigenstates. Instead, the convergence of Peaks 2 and 3 in Fig. 4e, which approaches a similar probe voltage after ~200 ns, suggests that these transient conductance features are associated with the relaxation of charged configurations during the $N-2 \rightarrow N-1$ recovery process.

Thus, we propose a physically plausible interpretation summarized in Fig. 4f. The common component of the resonance-position evolution may be associated with a time-dependent electrostatic realignment of the molecular junction during charge dissipation, including possible contributions from Coulomb renormalization and local charge redistribution. Meanwhile, the time-dependent change in the energy separation between the Peak 2 (T_1^{2+}) and Peak 3 (S_0^{2+}) states suggests that state-specific relaxation and tunneling pathways also contribute to the transient conductance spectra. In particular, the initially observed ~220 meV gap may reflect a differential stabilization of the T_1^{2+} state relative to S_0^{2+}, potentially arising from differences in their effective dipole responses to the local electric field."

To prevent any ambiguity, we have added a clarifying sentence to the caption of Fig. 4f: "The y-axis (E) represents the relative energy with respect to the Fermi level of the electrode."

Minor feedback:
1. Related to Fig. S13: I thank the authors for their explanations and agreeing that the change in lifetime is related to the energy broadening of the state. I believe that the energy broadening causes the population of the state to change, and thereby the observed lifetime of the average occupied state. Could the authors add that to the caption, for instance like: The lifetime initially exhibits an upward trend (between -0.5 V to -2 V) because of the energy broadening of the involved state, 'increasing the population of the excited state with increasing voltage'. However, once the excitation energy provided by exceeds the energy broadening of the excited state, the 'population and therefore the' lifetime reaches a plateau and remains almost entirely unchanged (between -2.5 V to -4 V).

Reply 2-4: Thanks for your suggestion. We agree that the observed change in lifetime is mechanistically linked to the population of the state driven by energy broadening. Accordingly, we have incorporated the discussion regarding the excited-state population into our manuscript and revised the caption of Fig. S13 (now renumbered as Fig. S15) as follows:



Supplementary Fig. 15 All-electronic pump-probe measurements of the BP molecule in device 3. a. Charge stability diagram of device 3 showing the differential conductance (dI_{SD}/dV_{SD}) as a function of bias voltage (V_{SD}) and gate voltage (V_G) at 30 K. **b**, Corresponding dependence of the probe current I_{probe} on the delay time as a function of gate voltage $V_{gate.}$ at a fixed pump voltage V_{pump} = −0.8 V. **c**, Many-body energy diagram illustrating gate-induced modulation, in which the energy gap between the $N-1$ and $N-2$ states decrease as a negative gate voltage V_G applied. **d**, Differential conductance (dI_{SD}/dV_{SD}) at V_{SD} = 0 V (blue line) and the lifetime of electrically excited states (red dots) as a function of continuous gate voltage V_G. The lifetime is extracted from the dynamics curves in Supplementary Figure 15b. The peak around $V_G \approx -1$ V in the differential conductance indicates the transition from the N state to the $N-1$ state. Under the condition of a fixed V_{pump}, sweeping the gate voltage V_G directly tunes the energy difference between the two different charge states. Correspondingly, the

transient dynamics become pronounced at $V_G < -1$ V, since the population of the $N-1$ state is negligible for $V_G > -1$V. The lifetime initially exhibits an upward trend (between −0.5 V to −2 V) because of the energy broadening of the involved state, which signifies a growing population of the excited state as the voltage increases. However, once the excitation energy provided by exceeds the energy broadening of the excited state, the population and therefore the lifetime reaches a plateau and remains almost entirely unchanged (between −2.5 V to −4 V).

2. Related to Fig. 2e, it would be helpful if the authors explicitly listed the probe pulse parameters in the caption of Fig. 2e (e.g. Vprobe = -1 V), even though they are, as the authors rightfully pointed out, indeed already mentioned at other places.

Reply 2-5: Thank you for the suggestion. We have explicitly listed the probe pulse parameter in the caption of Fig. 2e. The revised caption of Fig. 2e now reads as follows: "Corresponding dependence of the probe current I_{probe} on the delay time Δt as a function of pump voltage V_{pump} at a continuous V_G = –2.5 V. The amplitude of V_{probe} is fixed at 1 V, with the same polarity as the pump pulse".

Reviewer 3:

I have reviewed the extra comments made by reviewers 1 & 2 and the responses given by the authors. I believe that the quality and clarity of the manuscript have sufficiently improved as a result of the changes made by the authors. The authors' explanation is reasonable, though a minimal illustrative rate-equation sketch could still help address the recurring concern about timescales. I offer this only as a tentative suggestion and defer to the judgement of the other reviewers and the editor. I recommend the article for publication in Nature Communications.

Reply: Thanks for your recommendation and continued feedback. We agree that "a minimal illustrative rate-equation sketch could still help address the recurring concern about timescales", however, any minimal model we could build would have to rely on strongly under-constrained assumptions and arbitrary parameter fitting.