

Radical Enhanced Charge Transport in Single-Molecule Phenothiazine Electrical Junctions

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This manuscript is dedicated to the memory of Professor Thomas Wandlowski.

Abstract: We studied the single-molecule conductance through an acid oxidant triggered phenothiazine (PTZ) based radical junction using the Mechanically Controllable Break Junction technique. The electrical conductance of the radical state was enhanced by up to 200 times compared to the neutral state, with high stability lasting for at least two months and high junction formation probability at room-temperature. Theoretical studies revealed that the conductance increase is due to a significant decrease of the HOMO-LUMO gap and also the enhanced transmission close to the HOMO orbital when the radical forms. The large conductance enhancement induced by the formation of the stable PTZ radical molecule will lead to promising applications in single-molecule electronics and spintronics.

Investigations of charge transport through single molecules provide vital information for the design of materials for next-generation electronic devices.^[1] Recently, all-organic radical

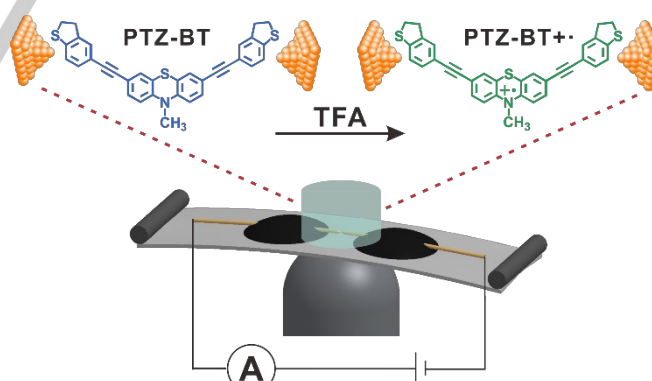
species have raised broad interest as the unpaired electron can lead to novel quantum phenomena for the electronics properties tuning,^[2] such as Kondo effects,^[3] quantum interference^[4] and magnetoresistive effects.^[5] However, although some pioneering studies investigated the charge transport through radicals using molecular assemblies^[5a, 6] or under ultra-high vacuum and cryogenic environment,^[3b, 5b] the seeking of appropriate molecular radicals for the fabrication of stable and highly conductive single-molecule devices remained as a major challenge for applying molecular radicals for future electronics devices.

The phenothiazine (PTZ) system can undergo one-electron oxidation on the nitrogen atom to form a radical cation (PTZ^{•+})^[7] with accompanying significant color change in solution via adding acid oxidant such as trifluoroacetic acid (TFA) under ambient conditions. More interestingly, the butterfly structure of the PTZ became more planar for the radical cation with electron density delocalized over the whole molecule including the central ring.^[8] Such prominent changes in the electronic properties of the PTZ radicals have received increasing research interests in organic light-emitting diodes,^[9] and also offer promising applications in the radical based molecular electronics devices.

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Scheme 1. Schematic of MCBJ setup and radical trigger reaction of PTZ derivative.

Herein, we study the single-molecule conductance of a PTZ derivative and its corresponding radical cation using the Mechanically Controllable Break Junction (MCBJ) technique^[10] in a mixed tetrahydrofuran/1,3,5-trimethylbenzene (THF/TMB, 1:4 v/v) solution at room temperature, as shown in Scheme 1. Prominent conductance signals of both the PTZ derivative and its

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corresponding radical cation are observed with a large conductance enhancement of up to 200 times for the radical state. Theoretical studies also reproduced the results that the radical state possesses a significantly higher electrical conductance compared with the neutral state because of significant electronic structural changes.

The PTZ derivative (10-Methyl-PTZ) named as **PTZ-BT** was designed and synthesized with dihydrobenzo[*b*]thiophene (BT) as the anchoring groups (See Supporting Information (SI) section 1 for synthetic details).^[11] The radical cation 10-Methyl-PTZ^{•+} named as **PTZ-BT^{•+}** was triggered upon adding 20% volume TFA into THF/TMB solution of the neutral **PTZ-BT**.^[12] To confirm the existence of the radical cation, UV-Vis absorption and Electron Spin Resonance (ESR) spectra were used to monitor the changes after TFA addition. The light-green solution of **PTZ-BT** turned pink immediately after the addition, and an absorption band around 518 nm emerged, as shown in Figure 1a. This absorption band suggested a $\pi \rightarrow \pi^*$ transition, which has been shown previously to be a signature of the phenothiazine radical cation.^[12d, 13] Furthermore, Figure 1b shows the ESR spectra of the solution of **PTZ-BT** before and after adding TFA: a distinct radical signal with 6 hyperfine splitting lines is observed after the addition. This splitting pattern, with *g* values close to 2.0051, is consistent with the literature data for a single unpaired electron on the nitrogen atom of the PTZ ring, suggested the generation of **PTZ-BT^{•+}**.^[12a, 14]

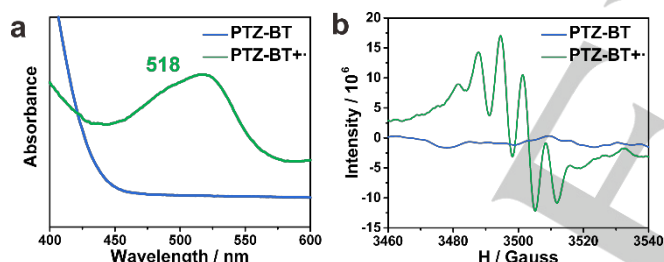


Figure 1. The (a) UV-Vis absorption spectra and (b) ESR spectra of PTZ species in THF/TMB mixed solution, before (blue) and after (green) the addition of TFA.

Single-molecule conductances were measured using the MCBJ technique in the mixed THF/TMB solution as mentioned above with a 0.1 mM concentration of the phenothiazine derivatives, and 100 mV bias voltage was applied between the two electrodes (See SI section 2 for more details of conductance measurements).^[10a, 10b, 15] Figure 2a shows the typical conductance traces of **PTZ-BT** and **PTZ-BT^{•+}**, both of the states exhibited clear molecular plateaus after discrete G_0 steps (where G_0 is the conductance quantum which equals $2e^2/h$), which suggests a gold atomic chain is pulled out then a molecular junction is formed.^[16] Although those curves of **PTZ-BT^{•+}** showed higher tunneling background due to the higher ion concentration from acid, conspicuous and stable conductance plateaus can be observed. Figure 2b shows the conductance histograms of both the neutral **PTZ-BT** and its corresponding radical cation states **PTZ-BT^{•+}**, each was constructed from two thousand individual conductance traces from Figure 2a. Statistical results exhibited

the conductance increases from the neutral state of **PTZ-BT** as $10^{-5.1} G_0$ ($7.94 \times 10^{-6} G_0$) to the radical state of **PTZ-BT^{•+}** as $10^{-2.8} G_0$ ($1.58 \times 10^{-3} G_0$), which suggest a remarkable conductance enhancement of up to 200 times. Control experiments of measuring merely TFA, and the tolane with BT anchors mixed with TFA suggested that the conductance changes are neither from the TFA itself nor from the solvent tuning effect (See Figure S3 and S4 of SI for more details).^[16]

The high enhancement ratio (200 times) of PTZ radical conductance even exceeded the highest enhancement ratio of the radical junction of the polychlorotriphenylmethyl radical SAM monolayer^[6] recently reported by Yuan *et al.*, which shows an enhancement ratio up to 100 times for the radical molecule comparing with the neutral one. More importantly, the enhanced conductance of the radical state of PTZ is even higher than that of the widely studied fully-conjugated oligophenyleneethynylene-3 (OPE3-SH, $10^{-3.7} G_0$)^[17] and even close to OPE2 (OPE2-SH, $10^{-2.8} G_0$),^[17a, 18] although **PTZ-BT^{•+}** has a slightly longer molecular length than OPE3 (~ 2.0 nm), and is much longer than OPE2 (~ 1.3 nm).^[17a] The comparison suggests that the PTZ core at the radical state is one of the most conductive molecular building blocks.

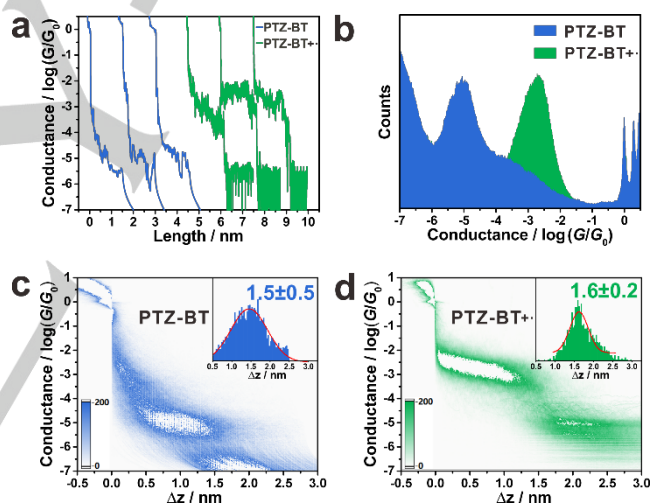


Figure 2. (a) Typical measured conductance distance traces of phenothiazine derivative **PTZ-BT** and its corresponding triggered radical cation **PTZ-BT^{•+}**. (b) conductance histogram comparisons between the both states before and after TFA addition. All-data-point 2D conductance versus relative distance (Δz) histogram and relative displacement distribution (inset) of (c) **PTZ-BT** and (d) **PTZ-BT^{•+}**, the conductance ranges to determine the relative displacement distribution are from $10^{-0.3}$ to $10^{-6.0} G_0$ for **PTZ-BT** and from $10^{-0.3}$ to $10^{-4.5} G_0$ for **PTZ-BT^{•+}**, respectively.

To further extract the effect of configuration changes on the charge transport through PTZ molecules, two-dimensional conductance-distance histograms^[10a, 19] were constructed for each state without any data selection, as shown in Figure 2c and Figure 2d, with each of their relative displacement distributions shown as the upright insets. All the histograms showed unambiguous conductance clouds, indicating a high junction formation probability. It is found that the traces of **PTZ-BT** start with the direct tunnelling feature before the molecular plateau,^[20] while the **PTZ-BT^{•+}** conductance plateau appeared immediately

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after the rupture of gold-gold contact. The relative displacement distribution enlarged very slightly from the neutral state into the radical state (1.5 nm of **PTZ-BT** to 1.6 nm of **PTZ-BT^{•+}**), for which the statistical range was from $10^{-0.3}$ to $10^{-6.0}$ G_0 for **PTZ-BT** and from $10^{-0.3}$ to $10^{-4.5}$ G_0 for **PTZ-BT^{•+}**, respectively. When adding the 0.5 nm snap-back distance,^[10a, 21] the length of the molecular junction is 2.0 and 2.1 nm for **PTZ-BT** and **PTZ-BT^{•+}**, respectively, which are slightly less than the maximum possible values, based on the computed molecular lengths of 2.31 nm and 2.33 nm for **PTZ-BT** and **PTZ-BT^{•+}** obtained from DFT simulations, respectively (See Figure S6-1 of SI for more details). These data suggest that these PTZ derivatives, especially the PTZ radical cation, possess relatively rigid structures to endure almost full stretching before junction breakage. The DFT simulations also suggest that the neutral and radical cation states have very similar molecular structures, with the dihedral angle of the PTZ core increased slightly from **PTZ-BT** to **PTZ-BT^{•+}** (See Figure S6-2 of SI for more details).^[8b, 22]

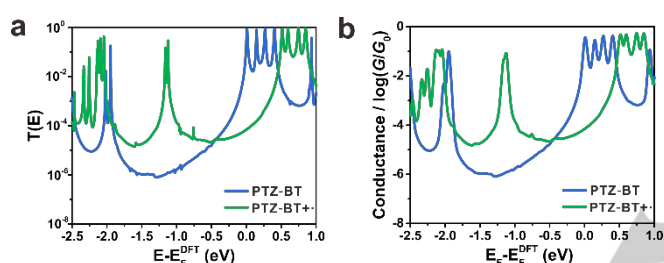


Figure 3. (a) Averaged spin-up and spin-down transmission coefficients of the two states, (b) room-temperature electrical conductance over a range of Fermi energies of two states. The blue lines refer to **PTZ-BT** and green to **PTZ-BT^{•+}**, respectively.

Such a small conformational change cannot explain the large conductance enhancement. To understand the radical-enhanced charge transport phenomena, we used the density functional theory code SIESTA^[23] to optimize the gold-molecule-gold junction geometry, and calculated the DFT mean-field Hamiltonian of the **PTZ-BT** molecules attached to two gold leads (with TFA placed close to **PTZ-BT** molecule for **PTZ-BT^{•+}**). The GOLLUM quantum transport code,^[24] was then used to obtain the electron transmission coefficient $T(E)$ and room-temperature electrical conductance (See SI section 6-2 for more details). As shown in Figure 3, the HOMO-LUMO gap decreases from ~ 2 eV for **PTZ-BT** (blue curve) to ~ 1.6 eV for **PTZ-BT^{•+}** (green curve), which is also confirmed by the red-shift of the UV-Vis spectra from Figure 1a.^[25] The decrease of the HOMO-LUMO gap with approximately the same tunnelling distance (as shown in Figure 2c, 2d and Figure S6-1 in SI) leads to significant conductance enhancement due to the lower tunnelling barrier.^[6] Moreover, it is also found that the transmission of **PTZ-BT^{•+}** is significantly higher than that of **PTZ-BT** within a wide energy level range close to the HOMO of **PTZ-BT** (from -1.2 eV to -1.8 eV) and **PTZ-BT^{•+}** (from -0.5 eV to -1.1 eV). Previous studies have shown that the charge transport through the molecules with BT or thiol anchors are dominated by the HOMO theoretically and experimentally.^[11, 26] Although the exact alignment of the Fermi energy is still difficult

to determine theoretically (See SI section 6-2 and 7 for more details and discussion),^[16b, 21b, 27] the calculation still suggested that **PTZ-BT^{•+}** exhibited higher conductance than **PTZ-BT** within the wide range of HOMO dominated energy level. The agreement between the calculation and the single-molecule conductance measurements suggested that the conductance enhancement originates from the significant drastic electronic structural changes of the PTZ core as the radical cation forms.

To further examine the long-term stability of the PTZ radical in solution, Figure 4 shows the conductance measurements of the **PTZ-BT^{•+}** solution every 12 hours for two days, and the result from the measurement of the same solution after 2 months' storage (See Figure S5-1 of SI for more details). The conductance of **PTZ-BT^{•+}** remained constant, which implies that the radical cation can exist at least for more than two months at room temperature in solution. The obtained UV-Vis spectra also revealed the presence of a radical species after long-period storage (See Figure S5-2 of SI for more details). Since organic radicals which consist of light elements such as H, C, N and S are promising materials due to the low spin-orbit coupling, they possess the potential to realize long spin relaxation times to enhance the stability of molecular devices.^[2] Hence, due to the delocalization of the electron density through the phenothiazine radical core, the energy of the corresponding frontier molecular orbitals of the PTZ radical will be significantly lowered, therefore the stability of the radical system will be enhanced.^[12a]

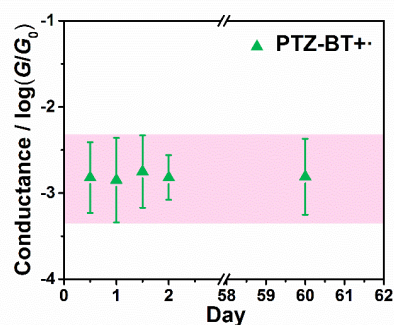


Figure 4. Measured conductance results of the radical cation **PTZ-BT^{•+}** during two days and even two months after adding TFA. The light pink area suggests the long term stability of the single-molecule conductance of the PTZ radical.

In summary, we investigated the charge transport properties through a room temperature stable radical system with a phenothiazine core using single-molecule conductance measurements and density functional theory. Up to 200 times conductance enhancement has been observed for the radical state compared to the neutral state, with high stability and junction formation probability. DFT simulations show that the conductance increase is due to a significant decrease of the HOMO-LUMO gap and enhanced transmission close to the HOMO orbital when the radical forms. The significant conductance enhancement from the formation of the radical at room temperature leads to promising applications of PTZ molecules for single-molecule electronics, optoelectronics and spintronics studies.

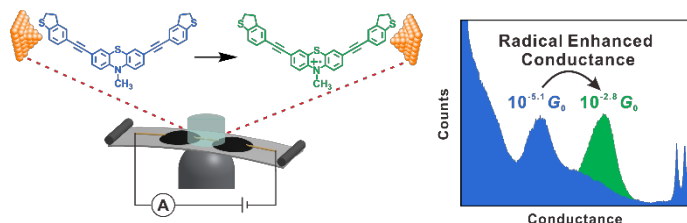
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Keywords: charge transport • radical cation • molecular electronics • single-molecule junctions

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Single-molecule conductances of phenothiazine radicals have been measured using Mechanically Controllable Break Junction technique. Triggered by acid oxidant, the radical cation of phenothiazine enhances the charge transport property by up to 200 times with high stability and high junction formation probability at room-temperature, which leads to promising applications in single-molecule electronics and spintronics.

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