Switching of Charge Transport Pathways via Delocalization Changes in Single-Molecule Metallacycles Junctions

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Supporting Information

ABSTRACT: To explore the charge transport through metall-a-aromatics building blocks, three metallacycles complexes were synthesized, and their single-molecule conductances were characterized by using mechanically controllable break junction technique. It is found that the conductance of the metallacycles junction with phosphonium group is more than 1 order of magnitude higher than that without phosphonium group. X-ray diffraction and UV−vis absorption spectroscopy suggested that the attached phosphonium group makes metallacycles more delocalized, which shortened the preferred charge transport pathway and significantly enhanced the single-molecule conductance. This work revealed that the delocalization of metalla-aromatics could be used to switch the charge transport pathway of single-molecule junctions and thus tune the charge transport abilities significantly.

State-of-art molecular electronics explores the charge transport through metalla-aromatics building blocks bridged between nanogap electrodes. To date, most of the building blocks investigated are traditional aromatic frameworks, such as benzene derivatives, porphyrins, ferrocene derivatives, and fullerenes. Metalla-aromatics are novel aromatic frameworks with unique electronic and photonic properties, which are derived from the replacement of a (hydro)carbon unit with a transition-metal fragment in conventional aromatic frameworks. Recently, the successful synthesis of a stable metalla-aromatics system, metalla-pentalyne and metalla-pentalene, provided us with the possibility to investigate the charge transport through metalla-aromatics at the single-molecule scale. The dπ−pπ conjugation in metallacycles offers a new chance to explore a new phenomenon and quantum effect in the charge transport through the novel molecular building blocks.

Single-molecule conductance measurement techniques, such as scanning tunneling microscopy (STM) break junction and mechanically controllable break junction (MCBJ), have been demonstrated as promising tools to reveal the charge transport pathway of single-molecule junctions. Our recent studies show the conductance of single-molecule junction highly depends on the connectivity and charge transport pathway through aromatic system due to the quantum interference effect. The single-molecule charge transport through metallacycles has not been studied yet, and the electron delocalization effect of metalla-aromatics may offer a unique opportunity to tune the pathway in metallacycles systems.

In this Communication, we studied the charge transport through single-molecule osmacycle junctions using mechanically controllable break junction technique, as shown in Figure 1. Three osmacycle complexes were designed and synthesized with two terminal anchors for single-molecule conductance measurement. It is found that the osmacycles provide high charge transport ability. More importantly, the osmapentalene derivatives with phosphonium group has the conductance more than 1 order of magnitude higher than that without phosphonium group. X-ray crystallography suggested that the attached phosphonium group introduced the delocalization effect into the osmapentalene ring, which shortened the preferred electron pathway and significantly enhanced the single-molecule conductance.

Scheme 1. Synthesis Route of Complexes 2, 3, and 4

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trace of pure solvent and complexes conductance-distance traces were recorded for each molecule thiol (DDT) that have similar length of charge transport.

The conductance of complex formation of fused osmafrica improved the degree of magnitude lower than which indicated that the conductance of rupture of gold quantum.

Figure 2. For all histograms, clear conductance peaks at 0.1 mM solution of target molecules were prepared in a mixture of tetrahydrofuran (THF) and 1,3,5-trimethylbenzene (TMB) solvent (v:v = 1:4). The conductance of complex 2 and 3, and 4 were characterized by nuclear magnetic resonance (NMR), elemental analysis (EA), and high-resolution mass spectrometry (HRMS).

Single-molecule conductance measurements of complexes 2–4 were carried out using mechanically controllable break junction technique. 0.1 mM solution of target molecule were prepared in a mixture of tetrahydrofuran (THF) and 1,3,5-trimethylbenzene (TMB) solvent (v:v = 1:4). ~2000 individual conductance-distance traces were recorded for each molecule for further statistical analysis. Figure 2a shows typical individual traces of pure solvent and complexes 2–4. For each complex, pure solvent experiment without target molecule was carried out first to check the cleanliness and also for the calibration of the displacement. It is found that there is a sharp drop after the rupture of gold–gold atomic contact at conductance quantum $G_0$ due to the snap back effect of the gold–gold contact. After that, the conductance traces in pure solvent showed exponential decay. With respect to complexes 2 and 3, it was observed that conductance plateau appeared at $10^{-5}$ and $10^{-6} G_0$, respectively, whereas for complex 4, there is only pure tunneling curve observed without clear conductance plateau above the noise level of $10^{-8} G_0$.

The corresponding conductance histograms are shown in Figure 2b. For all histograms, clear conductance peaks at $G_0$ and its multiples are found, which are attributed to the gold–gold atomic contacts. Besides the $G_0$ peaks, there are also clear conductance peaks observed for 2 and 3 located at $10^{-4.6}$ and $10^{-6.3} G_0$ respectively. However, no significant conductance feature could be found for 4 above the noise level of $10^{-8} G_0$ which indicated that the conductance of 4 is at least 1 order of magnitude lower than 3. This finding suggested that the formation of fused osmafrica improved the degree of conjugation, thus resulted in the enhanced single-molecule conductance. The conductance of complex 2 is in between oligo (phenylene ethynylene)-3 (OPE-3) and 1,10-decane-di-thiol (DDT) that have similar length of charge transport pathway, of which the conductances are $10^{-3.9} G_0$ and $10^{-4.9} G_0$ respectively.

More interestingly, it is found that the attached phosphonium group significantly tunes the conductance by more than 1 order of magnitude. Previous experimental and theoretical investigations demonstrated substituent groups are able to influence single-molecule conductance through the effects of side chain, aromaticity, photochromic effect, and ambipolar transport of molecules. However, the conductance enhancement from the phosphonium group is much higher than those reported, suggesting a new mechanism accounting for the charge transport tuning through the metallacycles system.

To exclude the conductance differences from configurational changes, we constructed the two-dimensional (2D) conductance-displacement histograms for three complexes. It is found that for complexes 2 and 3, the 2D histograms show clear molecular plateaus at around $10^{-5}$ and $10^{-6} G_0$ with similar lengths. For molecule 3, it is found that most of the traces shows transitions at around 0.5 nm, indicating the evolution of charge transport from direct tunneling to molecular tunneling. However, for complex 4, no clear molecular plateau can be found, which is in good agreement with the conductance histogram analysis, which suggest the phosphonium without a lone pair of electrons could not act as anchors to provide the charge transport pathway for these molecules (see SI section 7 for more details). The displacement distribution analysis shown in Figure 3d demonstrates that the molecular junctions of complexes 2 and 3, as given in Figure 3a,b, are stretched to fully elongated configurations, suggesting the conductance differences between complexes 2 and 3 are not from the configurational differences between their molecular junctions.

To further understand the conductance differences among three complexes, the UV–vis absorptions of complexes 2, 3, and 4 are summarized in Figure 4. To understand the spectra, we performed time-dependent density functional theory (TD-DFT) calculations on the cationic part of 2, 3, and 4 at the B3LYP/6-31G(d) level (see SI section 3 for more details). The theoretical spectra are consistent with the experimental results. The absorption band detected at $\lambda = 597$ and 528 nm of complex 2 can be assigned to the electronic transitions...
HOMO→LUMO and HOMO-1→LUMO. And the maximum absorption of complex 3 and 4 at λ = 545 and 557 nm can be also ascribed to their HOMO→LUMO transitions. The maximum absorption of complex 2 (597 nm) is red-shifted by 40 nm compared with that of complex 3 (545 nm), which suggests that complex 2 have a more delocalized structure than complex 3. The maximum absorption of complex 4 is 557 nm, which is blue-shifted by 40 nm compared with that of complex 2, suggesting that the conjugation length was reduced while the osmapuran ring opened.

The X-ray diffraction offers the direct access to characterize the delocalization effect, and the molecular structures of the three compounds are shown in Figures 5a,b and S22–24. The osmium center in complexes 2 and 3 are seven-coordinate with an approximately pentagonal bipyramidal geometry. The osmapentalenofuran unit and the fused lactone ring in complexes 2 and 3 are almost coplanar, reflected by the mean deviation from the least-squares plane (0.078 Å for 2 and 0.067 Å for 3). All of Os—C bond lengths in complex 2 (Os1—C1 2.152(3), Os1—C1 2.056(3), Os1—C4 2.115(3), Os1—C7 2.121(3) Å) are within the range of those reported for osmapentalene derivatives (1.926–2.175 Å). In the osmapentalene unit of complex 2, the C—C bond-lengths are in the range of 1.384(5)–1.426(5) Å, without significant C—C bond-length alternation, as expected for a delocalized structure. Whereas, in complex 3, the C—C bond lengths (1.363(6)–1.427(5) Å) within the osmapentalene unit show a significant short—long bond alternation (specially, the bold bond-lengths in Figure 5b), indicating a relatively localized structure compared to 2. Due to the destructive quantum interference effect from the C6—C7 double bond, charge transport pathway of complex 3 can hardly go through the Os1—C7 bond; alternatively, it prefers the pathway around the metallapentalene rings (the red pathway in Figure 5b).

As shown in Figure 5c, the crystal data indicates that, compared to complex 3, there is a higher degree of electronic delocalization in complex 2 with contributions from 2, 2a, and 2b, which suggests that the phosphonium group can participate in resonance structures to enhance the double bond character of Os1—C7. The NMR data of complexes 2 and 3 are consistent with the solid state structure. In 13C{1H} NMR spectra, the signal for C7 located at 201.4 ppm for complex 2 and 187.8 ppm for complex 3, and the signal for C1 located at 255.3 ppm for complex 2 and 260.7 ppm for complex 3. These results suggest that C7 in complex 2 show more carbene character than C7 in complex 3, thus indicating the resonance forms 2a and 2b provide significant contribution to the overall structure of the complex 2. Consequently, the charge is able to transport through the Os1—C7 double bond with a shorter pathway (red pathway in Figure 5a) than the one through around the metallapentalene rings, leading to a much higher single-molecule conductance. On the other hand, the osmium in complex 4 is six-coordinate in twist octahedral geometry and shared by two fused five-membered rings. On coordination of Cy—N=CM to the osmium center of 2 the Os—C12 bond is broken and the osmapuran ring is opened (Scheme 1). This breaks the charge transport pathway through C12 and diverts it through the oxygen atom. As this is linked to adjacent atoms by two essentially single bonds, the conjugation through this new charge transport pathway is considerably weaker.

To conclude, we present the first experimental investigation of the charge transport through metallacycles type single-molecule junctions using the MCBJ technique. It is shown that the single-molecule conductance of the metallacycles is comparable with other conjugated systems. More importantly, the attached phosphonium group in the metallacycles provides the access to tune the metallacycles by delocalization effect, which leads to the conductance difference higher than 1 order of magnitude. The switching of localized and delocalized structure of the metallacycles is confirmed by the UV—vis absorption spectroscopy and X-ray diffraction. This work demonstrates that metallacycles complexes could be highly promising building blocks and thus further increase the diversity of molecules for future molecular electronics, and also suggests that the delocalization effect could offer a new avenue to tune the charge transport in molecular materials and devices.

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Figure 5. (a,b) Molecular structures of the cationic parts of 2 (a), and 3 (b) drawn with 50% probability. The phenyl groups in triphenylphosphine (PPh3) moieties are omitted for clarity. The ESD values are given in parentheses. (c) Resonances structures of 2. The red lines represent charge transport pathway.
Compounds syntheses procedures, X-ray characterization of compounds, UV−vis absorption spectra, DFT computational details, mechanically controllable break junction and data analysis, and control experiment of compound 1 (PDF)

Crystallographic data for 2, 3, and 4 (CIF)

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**REFERENCES**


