

# Tuning the contact conductance of anchoring groups in single molecule junctions by molecular design†

Jakub Šebera,<sup>a</sup> Marcin Lindner,<sup>‡b</sup> Jindřich Gasior,<sup>a</sup> Gábor Mészáros,<sup>c</sup> Olaf Fuhr,<sup>b</sup> Marcel Mayor,<sup>b,d</sup> Michal Valášek,<sup>b</sup> Viliam Kolivoška<sup>\*a</sup> and Magdaléna Hromadová<sup>id</sup><sup>\*a</sup>

A tetraphenylmethane tripod functionalized with three thiol moieties in the *para* position can serve as a supporting platform for functional molecular electronic elements. A combined experimental scanning tunneling microscopy break junction technique with theoretical approaches based on density functional theory and non-equilibrium Green's function formalism was used for detailed charge transport analysis to find configurations, geometries and charge transport pathways in the molecular junctions of single molecule oligo-1,4-phenylene conductors containing this tripodal anchoring group. The effect of molecular length ( $n = 1$  to 4 repeating phenylene units) on the charge transport properties and junction configurations is addressed. The number of covalent attachments between the electrode and the tripodal platform changes with  $n$  affecting the contact conductance of the junction. The longest homologue  $n = 4$  adopts an upright configuration with all three *para* thiolate moieties of the tripod attached to the gold electrode. The contact conductance of the tetraphenylmethane tripod substituted by thiols in the *para* position is higher than that substituted in the *meta* position. Such molecular arrangement is highly conducting and allows well-defined directional positioning of a variety of functional groups.

## Introduction

Molecular electronics aims at realizing functional electronic devices relying on molecular building blocks. A robust and directional contact between molecular components and a metallic electrode is viewed as an essential prerequisite for fabricating well-defined architectures for molecular electronic applications. Multipodal platforms were developed recently to establish a directional attachment of molecules to metallic surfaces.<sup>1,2</sup> Tripodal scaffolds are their most common representatives and include triazatriangulene,<sup>3–5</sup> trioxatriangu-

lene,<sup>6</sup> cyclohexane trithiol,<sup>7</sup> adamantane,<sup>8–11</sup> tris(azobenzyl) amine,<sup>12</sup> spirobifluorene,<sup>13–16</sup> tetraphenylmethane<sup>17–22</sup> and tetraphenylsilane<sup>23,24</sup> moieties.

The principal function of molecular electronic components is the transport of electric charge. The latter may be investigated at the single molecule level by various approaches including the scanning tunneling microscopy break junction (STM-BJ) technique.<sup>25</sup> The charge transport properties of single molecule electronic components based on tripodal platforms were investigated in several recent contributions focusing on elucidation of the charge transport mechanism<sup>3,21,24</sup> and the analysis of molecular junction (MJ) geometries.<sup>14–16,21,22</sup> Theoretical analysis of the charge transport in MJs used the combination of density functional theory (DFT) and non-equilibrium Green's function (NEGF) formalism. Furthermore, the DFT/NEGF approach was successfully employed to examine the charge transport in molecular electronic elements supported by tripodal platforms including triazatriangulene,<sup>3</sup> adamantane,<sup>11</sup> spirobifluorene<sup>14–16</sup> and tetraphenylmethane<sup>19,21</sup> moieties.

The tetraphenylmethane moiety possessing three thiol groups as anchors has recently attracted considerable attention as a potential platform to support molecular electronic components.<sup>17,18,21,22</sup> Molecular conductors based on this plat-

<sup>a</sup>J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, 18223 Prague, Czech Republic. E mail: hromadom@jh inst.cas.cz, viliam.kolivoska@jh inst.cas.cz

<sup>b</sup>Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, P. O. Box 3640, 76021 Karlsruhe, Germany. E mail: michal.valasek@kit.edu

<sup>c</sup>Research Centre for Natural Sciences, HAS, Magyar tudósok krt. 2, H 1117 Budapest, Hungary

<sup>d</sup>Department of Chemistry, University of Basel, St. Johannis Ring 19, 4056 Basel, Switzerland

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9nr04071d

‡Present address: Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01 224 Warsaw, Poland.

form possessing 1,4-phenylene as a repeating unit in the principal molecular backbone capped with the  $-\text{CN}$  moiety were found to show unique behavior when chemisorbed on the Au(111) surface. At cryogenic temperatures, high-resolution STM imaging revealed that self-assembled monolayers are formed with molecules lying parallel to the surface.<sup>17</sup> At ambient temperature, electrochemical reductive desorption experiments combined with DFT molecular modeling revealed that the same conductors form densely packed self-assembled monolayers with molecules standing upright on the Au(111) surface, with all three thiolate moieties being involved in the covalent attachment to the surface.<sup>21</sup> STM-BJ measurements further discovered that molecules form highly conductive single MJJs in which the electric charge is transported through the tripodal platform, while the principal molecular axis and top  $-\text{CN}$  moiety are beyond the transport pathway. This behavior was explained by a relatively weak interaction between the gold STM probe and the top  $-\text{CN}$  moiety of the molecule.<sup>21</sup>

In this work, we aim at investigating single molecule charge transport through tetraphenylmethane based molecular conductors **1** to **4** containing four thiolate anchoring groups with a possibility of three of them forming one tripodal anchor (see Scheme 1). We are the first to determine the contact conductance value for a tripodal platform and demonstrate favorable tuning of the contact conductance of the anchoring group that leads to an increase of the single molecule conductance by more than one order of magnitude thanks to the involvement of three parallel transport pathways. So far, characteristics of systems involving parallel transport pathways have been reported only for molecules with two identical transport channels, with non-additive conductance behavior being observed in all cases. Xing *et al.*<sup>26</sup> investigated the charge transport characteristics of phenylene-ethynylene based molecular conductors terminated with monopodal thiol and bipodal carbodithioate linkers concluding that the dipodal attachment enhances the electronic coupling (contact conductance) of the junction by a factor of five compared to the monopod. Interestingly, Tivanski *et al.*<sup>27</sup> discovered that the conductance of junctions containing biphenyl based conductors capped by the above-mentioned two moieties differs only by  $\approx 35\%$ . Kiguchi *et al.*<sup>28</sup> devised and investigated molecular conductors based on 5-sulfanyltiophen-2-ylethynyl anchors with either

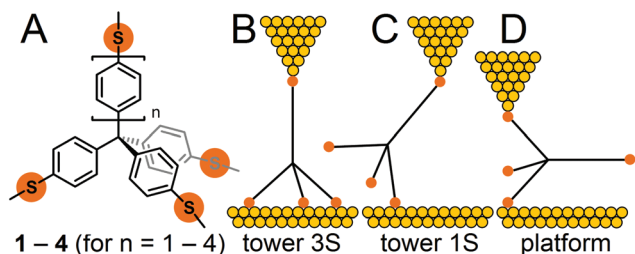
one or two conductance pathways, observing that the single molecule conductance values of the two derivatives differ by a factor of five. Vazquez *et al.*<sup>29</sup> compared the experimental and theoretical single molecule conductance values for molecular conductors with single and double conductance pathways. Positive non-additivity was ascribed to constructive quantum interference in molecules with the doubled backbone. Seth *et al.*<sup>30</sup> designed, investigated and theoretically analyzed single molecule breadboard circuits based on a bis-terpyridine molecule, assigning single molecule conductance states to the underlying constituent circuits. Hansen *et al.*<sup>31</sup> used a theoretical approach to compare the charge transport in conjugated molecules with simple and multiple connections to electrodes. Magoga and Joachim<sup>32</sup> provided a general analytical solution for the conductance of single molecules composed of parallel transport pathways. They demonstrated that for the conductor with  $p$  identical pathways, the overall conductance is proportional to  $p^2$  (quadratic superposition law). The first example of the constructive quantum interference was reported by Vazquez *et al.*<sup>29</sup> The present work aims to test this general theory as well.

## Experimental

All four compounds **1** to **4** were synthesized as thioacetates to prevent the oxidation of thiolate anchoring groups by atmospheric oxygen. Their synthesis and characterization are given in detail in the ESI.†

Single molecule conductance measurements of **1** to **4** were carried out by the *in situ* STM-BJ technique in mesitylene solvent. Prior to each measurement, thioacetates were converted to thiols by the addition of triethylamine. The current response as a function of distance  $\Delta z$  between a gold substrate and probe in the absence and presence of molecules was monitored. Repetitive formation and breaking of the junctions was performed and retraction curves (3000 to 5000 for each molecule) were further analyzed without any data selection. The approach and retraction rates of the probe were 360 and 36 nm s<sup>-1</sup>, respectively. The bias voltage between the substrate and probe electrodes was set to 260 mV. Electric current was converted to conductance  $G$  using Ohm's law. Conductance-distance traces for individual compounds were processed statistically to obtain 1D and 2D conductance histograms and plateau length histograms. The characteristic length of the MJJs was calculated as  $z_{\text{exp}} = \Delta z^* + z_{\text{corr}}$ , where  $z_{\text{corr}} = 0.4$  nm is a snap-back correction and  $\Delta z^*$  is the experimentally obtained molecular plateau length. Detailed description of experimental procedures, the STM-BJ setup and data analysis was reported previously.<sup>15,33</sup> Further experimental details are given in the ESI.†

The charge transport in single MJJs of the investigated compounds was further analyzed theoretically by combining DFT and non-equilibrium Green's function (NEGF) formalism. The theoretical junction conductance value  $G$  was derived from the value of the transmission function  $\tau(\epsilon_F)$  obtained at the Fermi level of electrodes by the Landauer approach using zero-bias



**Scheme 1** Chemical structure of the investigated compounds **1** to **4** for  $n = 1$  to  $4$  (A). Theoretically considered tower 3S (B), tower 1S (C) and platform (D) configurations of MJJs.

approximation<sup>34,35</sup> and applying the formula  $G = G_0 \times \tau(\epsilon_F)$ <sup>36,37</sup> where  $G_0$  is the conductance quantum equal to  $77.5 \mu\text{S}$  and  $\epsilon_F$  is the experimentally obtained Fermi energy of gold equal to  $-5.1 \pm 0.1 \text{ eV}$ .<sup>38</sup> Theoretical conductance was obtained for various geometrical MJ arrangements, which allowed experimentally obtained single molecule conductance features to be assigned to a particular charge transport pathway through the molecule.<sup>15,21</sup> The theoretical MJ length was obtained as  $L = z_{\text{theor}} - d_{\text{Au}}$ , where  $z_{\text{theor}}$  is the perpendicular distance of the planes of two gold electrodes involving the centers of surface atoms and  $d_{\text{Au}} = 0.25 \text{ nm}$  is the diameter of the gold atom. Further computational details are given in the ESI.†

## Results and discussion

Charge transport characteristics of single MJs of **1** to **4** were obtained by the STM-BJ technique in the solution of the respective molecules. For each compound, several thousands of individual junctions were formed and broken between the substrate and the probe. The obtained conductance–distance ( $G$  vs.  $\Delta z$ ) traces were processed by means of statistical analysis without any data selection.<sup>15</sup> The presented 1D conductance and 2D conductance–distance histograms depict the logarithm of junction conductance  $\log(G/G_0)$  referenced to the conductance quantum  $G_0$ . The results are demonstrated by taking the longest compound **4** as the representative of the investigated series (Fig. 1). The characteristics of all four derivatives complemented by their typical individual conductance–distance traces are shown in Fig. S18 to S21 in the ESI.†

Maxima observed in 1D conductance (Fig. 1A) and horizontal plateaus observed in the 2D conductance–distance (Fig. 1B) histograms at  $\log(G/G_0) \geq 0$  reflect the existence of nanojunctions involving one or a few gold atoms formed in the early stage of the junction evolution.<sup>39</sup> Breaking of the gold nanocon-

tacts upon pulling the electrodes apart leads to a sudden drop in the junction conductance value by two to three orders of magnitude. The presence of a molecule between electrodes gives rise to additional feature(s) in the range of measurable conductance values. This range is limited by the onset of the instrumental noise level at  $\log(G/G_0) \sim -6.5$  for our STM-BJ setup. For molecule **4** in Fig. 1, two molecular features centered at  $\log(G_{\text{H}}/G_0) = -3.9 \pm 0.6$  (red) and  $\log(G_{\text{L}}/G_0) = -5.6 \pm 0.5$  (green) were observed. The two values were obtained as maxima of the best baseline-corrected double Gaussian fit (Fig. 1A) and are further regarded as the single molecule conductance values of **4**. Master curves of features  $G_{\text{H}}$  and  $G_{\text{L}}$  were obtained by evaluating the weighted average of counts at  $\log(G/G_0)$  values as a function of  $\Delta z$  (black curves in Fig. 1B) and depict the characteristic evolution of MJs. Histograms constructed for molecules **2** and **3** (see Fig. S19 and S20 of the ESI†) show  $G_{\text{H}}$  or  $G_{\text{L}}$  features similar to **4** while a single feature  $G_{\text{H}}$  is observed for the shortest molecule **1** (see Fig. S18 of the ESI†).

Plateau length distributions (Fig. 1C and D) were constructed by plotting a horizontal cross-section through data-points in the 2D histogram negative to the  $G_{\text{H}}$  and  $G_{\text{L}}$  features. Both distributions show two maxima. Maximum at shorter distance represents tunneling through the solvent in the absence of molecule (not considered further). Maximum at longer distance (red/green) is related to the formation of single molecule junction. The characteristic MJ length  $\Delta z$  obtained by data fitting amounts to  $\Delta z_{\text{H}}^* = 0.7$  (red) and  $\Delta z_{\text{L}}^* = 1.7 \text{ nm}$  (green). These two values were used further to obtain the experimental MJ length  $z_{\text{exp}}^{\text{H}}$  and  $z_{\text{exp}}^{\text{L}}$  (see the Experimental section for details).

Fig. 2 summarizes the experimentally-obtained values of single molecule conductance  $\log(G_{\text{H}}/G_0)$  (A) and  $\log(G_{\text{L}}/G_0)$  (B) and MJ lengths  $z_{\text{exp}}^{\text{H}}$  (C) and  $z_{\text{exp}}^{\text{L}}$  (D) shown as filled symbols.

The presence of two conductance features  $G_{\text{H}}$  and  $G_{\text{L}}$  for **2** to **4** suggests that the charge transport through their single molecules involves more than one pathway. The DFT/NEGF

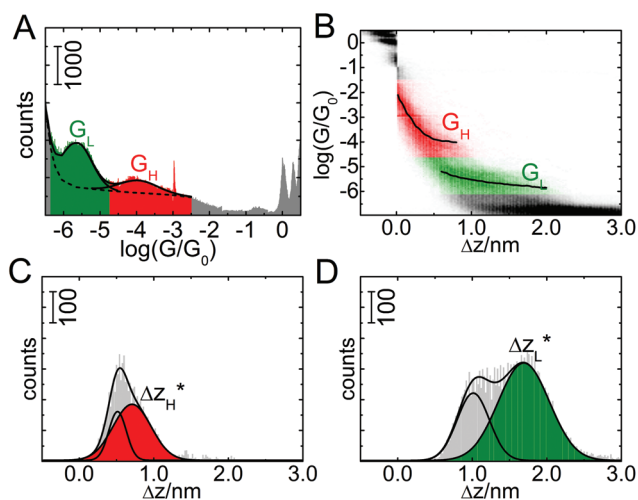


Fig. 1 1D conductance (A) and 2D conductance distance (B) histograms and plateau length histogram obtained for the  $G_{\text{H}}$  (C) and  $G_{\text{L}}$  (D) features shown for compound **4**.

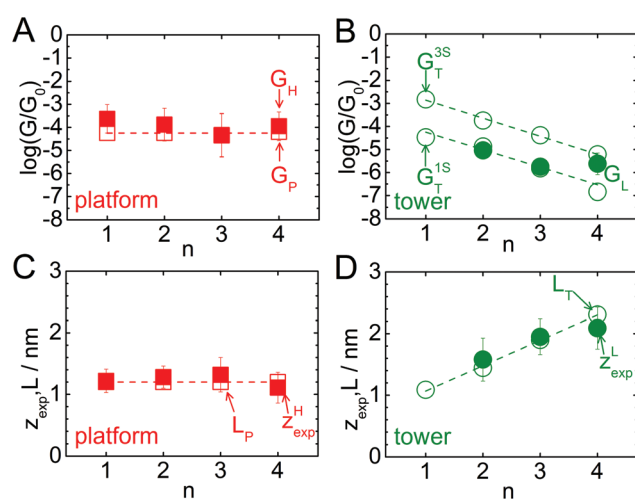


Fig. 2 Experimentally obtained (filled symbols) and theoretically predicted (empty symbols) values of the conductance (A, B) and length (C, D) of MJs as a function of  $n$ .

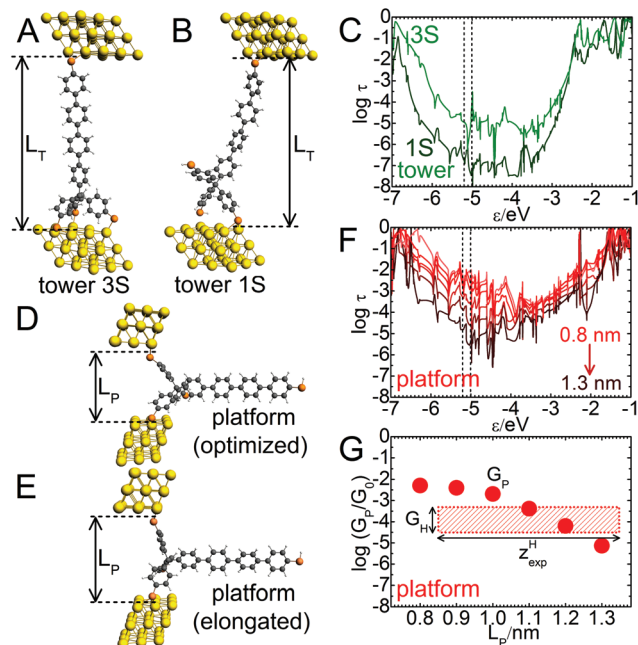
theoretical approach was applied to determine single molecule conductance values of MJs with varied transport pathways and geometries, aiming at finding the most probable configurations of MJs for experimental  $G_H$  and  $G_L$  features. In the theoretical analysis, the principal molecular axis was either considered as involved (“tower” configurations) or omitted (“platform” configurations) from the pathway. Tower configurations differ from each other in the number of covalent attachments between the platform and the electrode, considering either one (1S, Scheme 1C) or three (3S, Scheme 1B) thiolate-gold bonds. The tripod geometry comprising two thiolate-gold bonds is not computationally accessible due to restrictions on the charge neutrality of the system. Subtraction of three hydrogen radicals and formation of three gold-thiolate bonds including two from the tripod and one from the oligophenylene molecular wire would yield radical species. Experimentally this is not the case. Even though the theoretical analysis can deal with this problem by making adjustments to the MJ model to provide a closed-shell system, we did not follow this path. For this reason we did not treat theoretically the 2S tripod configuration. Optimized geometries of the 1S and 3S type of tower MJ configurations of **4** are shown in Fig. 3B and A. For platform configurations, the attachment of one thiolate-gold bond to each electrode is considered (Scheme 1D) and the distance between electrodes  $L_P$  (see the Experimental section for its exact definition) is left as a variable changing from 0.8 nm to 1.3 nm. Fig. 3D shows the optimized geometry of the platform configuration of **4** ( $L_P =$

1.0 nm), while Fig. 3E shows an example of the MJ geometry with an elongated electrode distance ( $L_P = 1.2$  nm). Transmission functions  $\tau(\epsilon)$  obtained for varied geometries of tower and platform MJ configurations of **4** are plotted in Fig. 3C and F. Fig. 3F shows changes in the transmission function  $\tau(\epsilon)$  as the length of the platform MJ configuration increases. Fig. S27 and S28 in the ESI† show a comprehensive list of transmission functions obtained for all MJ configurations and geometries of all four derivatives studied.

Fig. 3G compares the theoretical  $\log(G_P/G_0)$  values of **4** as a function of  $L_P$  (filled circles representing  $G$  values calculated from the transmission functions shown in Fig. 3F) with the experimental value of  $\log(G_H/G_0) = -3.9 \pm 0.6$  of **4** (dashed rectangle) suggesting that a good agreement is obtained for  $L_P = 1.2$  nm. This indicates that the experimentally achieved  $G_H$  state of MJs originates due to platform configurations with a slightly elongated electrode distance. The same conclusion was arrived at for all four derivatives (Fig. 2A) and is further corroborated by a perfect match between the theoretically predicted ( $L_P$ ) and experimentally obtained ( $z_{\text{exp}}^H$ ) MJ length values (Fig. 2C). A perfect agreement between experimental  $\log(G_L/G_0)$  and theoretical  $\log(G_T^{1S}/G_0)$  values of 2 and 3 (Fig. 2B) indicates that the  $G_L$  state of MJs involves tower configurations with the tripod attached to the electrode by one thiolate-gold bond (Scheme 1C). In contrast, a good match between the experimental  $\log(G_L/G_0)$  and theoretical  $\log(G_T^{3S}/G_0)$  conductance values observed for **4** confirms the attachment of the tripod to the electrode by all three thiolate-gold bonds (Scheme 1B and Fig. 3A).

It should be emphasized that for tower configurations, the comparison of the experimental  $z_{\text{exp}}^L$  and theoretical  $L_T$  lengths of MJs cannot differentiate between 1S and 3S geometries as the two arrangements have virtually the same MJ length (compare  $L_T^{1S}$  and  $L_T^{3S}$  values in Table S9†). The assignment of the geometry in the tower MJ configuration thus has to rely solely on the comparison of single molecule conductance values. Importantly, an excellent overall agreement between  $z_{\text{exp}}^L$  and  $L_T$  values and the linear proportionality of both characteristics to  $n$  (Fig. 2D) clearly demonstrate that tower MJs reach fully elongated geometries (Fig. 3A and B) in the  $G_L$  state of MJs as anticipated for thiolate anchoring moieties.<sup>40</sup>

The results of the DFT/NEGF analysis performed for the 1S and 3S geometries of the tower MJ configurations of **1** to **4** may be further used to quantify the coupling between the tripod and the gold electrode by comparing the contact conductance ( $G_c$ ) values for these two geometries. Assuming tunneling to be the operating charge transport mechanism, the conductance of a molecule is given by  $G_T = G_c e^{-L_T}$ , where  $\beta$  is a parameter describing the attenuation of the electric conductance through the molecular backbone (oligo-1,4-phenylene in this work). The values of  $G_c$  and  $\beta$  may be extracted by fitting the dependence of  $\ln G_T$  on  $L_T$  (see Fig. S29 in the ESI†). The contact conductance  $G_c$  values obtained for 1S and 3S geometries of tower MJs are given by  $G_c^{1S} = 0.39 \mu\text{S}$  and  $G_c^{3S} = 8.7 \mu\text{S}$ , leading to the ratio  $G_c^{3S}/G_c^{1S} = 22$ . This ratio is higher than the ratio of



**Fig. 3** Geometries of tower (A,B) and platform (D,E) configurations; transmission functions of tower (C) and platform (F) MJ configurations of **4**. Panel G shows the theoretical  $G_P$  values for the platform configuration as a function of  $L_P$  (filled circles) and comparison with the experimental  $G_H$  and  $z_{\text{exp}}^H$  values (dashed rectangle).

$G_C^{2S}/G_C^{1S} = 5$  extrapolated from the conductance values of oligo (phenylene-ethynylene) wires terminated with carbodithiol (2S) and thiol (1S) anchoring groups reported by Xing *et al.*,<sup>26</sup> thus confirming better charge transport properties of tripodal anchors compared to bipodal and monopodal anchors.

Single molecule anchoring by all three thiolate groups of the tripod leads to a significant increase of the conductance upon the formation of two additional sulfur-gold bonds (Fig. 3A-C). The obtained ratio of 22 is much higher than that predicted theoretically for three identical parallel charge transport pathways ( $p = 3$ ) by the quadratic superposition law ( $p^2 = 9$ ) and indeed confirms the constructive quantum interference.<sup>32</sup>

The obtained values of  $\beta^{3S} = 4.2 \pm 0.1 \text{ nm}^{-1}$  and  $\beta^{1S} = 4.4 \pm 0.4 \text{ nm}^{-1}$  for 1S and 3S tower geometries indicate that the coupling between the tetraphenylmethane tripod and the electrode has virtually no impact on the intrinsic electric conduction through the oligo-1,4-phenylene backbone. The two values of  $\beta$  fall within the range of values reported in the literature for oligo-1,4-phenylene based molecular wires ( $3.5\text{--}5.0 \text{ nm}^{-1}$ ).<sup>41</sup>

Additionally, we have a unique opportunity to compare the experimental conductance of the  $G_L$  state for oligo-1,4-phenylene molecular wires that contain the tetraphenylmethane tripod with thiolate anchors either in the *para* (molecule 4 of this paper) or in the *meta* position (molecule 4 reported by Koliřovřka *et al.*<sup>22</sup>). The experimental single molecule conductance value for the *para* connected molecule 4 is  $G_L^{para} = 2.0 \times 10^{-4} \mu\text{S}$  and that for *meta* is  $G_L^{meta} = 1.2 \times 10^{-4} \mu\text{S}$ . Theoretical  $\ln G_T^{3S}$  values for *para* and *meta* derivatives 1 to 4 were plotted against theoretical  $L_T^{3S}$  values (see Fig. S30 in the ESI†), which further corroborated our experimental finding giving a higher contact conductance value  $G_C^{3S}$  for *para* compared to the *meta* connected tripod. The single molecule conductance ratio  $G_L^{para}/G_L^{meta} = 1.67$  obtained for 4 in this work is higher than the ratio obtained for *para*- and *meta*-benzenedithiol (BDT)  $G_{BDT}^{para}/G_{BDT}^{meta} = 1.25$  reported in the literature.<sup>42</sup> The observed difference is most likely due to the involvement of three thiolate anchors in the covalent attachment of the tetraphenylmethane tripod to the electrode. A higher value of  $G_L^{para}$  compared to  $G_L^{meta}$  is consistent with the theoretical predictions considering quantum interference effects in substituted benzene cores.<sup>43</sup>

We have demonstrated that the experimentally observed transition in the tower MJ geometry of 2 and 3 on one hand and 4 on the other hand occurs due to a change in the number of covalent bonds with the electrode. Importantly, the change in the molecular design represented by the length of the oligo-1,4-phenylene backbone (1) allows tuning the contact conductance of the anchoring platform and (2) leads to the formation of favorable directional arrangement of the tripod on the gold surface (Fig. 3A) that involves three thiolate-gold covalent bonds. In such a configuration the principal molecular axis is directed towards the top of the molecular assembly and can potentially carry molecular electronic functional groups to be addressed by external stimuli such as light, a scanning probe or species dissolved in the solution bulk.

## Conclusions

The experimental STM-BJ approach and computational DFT/NEGF analysis were employed to investigate the single molecule charge transport in a series of conductors with the tetraphenylmethane tripodal platform supporting the wire composed of one to four 1,4-phenylene repeating units (compounds 1 to 4). Derivatives 2 to 4 show two distinct experimental single molecule features  $G_H$  and  $G_L$  unambiguously assigned to the theoretically modelled charge transport pathway solely through the tripod (platform configuration) and the entire molecule involving the wire (tower configuration), respectively.

A detailed theoretical configurational analysis of the  $G_L$  feature revealed that for derivatives 2 and 3 the tripodal platform is attached to the electrode by one thiolate anchor (1S) while all three sulfur atoms (3S) are in contact with the electrode in the case of the derivative 4.

The theoretically obtained  $G_T^{1S}$  and  $G_T^{3S}$  datasets further provided the contact conductance of the tripodal platform  $G_C^{1S}$  and  $G_C^{3S}$ . The values of  $\beta$  are nearly independent of the contact geometry, while a high ratio of  $G_T^{3S}/G_T^{1S}$  equal to 22 was found. This is much higher value than that predicted by the quadratic superposition law.<sup>32</sup> We also demonstrated that the contact geometry of the tripod is controlled by the molecular length. The geometry achieved for the derivative 4 allows an enhanced electronic communication and well-defined directional self-assembly of molecules on the electrode. The conductance of 4 is even higher than that of a molecule anchored to the gold electrode by the tetraphenylmethane tripod containing thiols in the *meta* position.<sup>22</sup> The molecular architecture of 4 may thus be employed as a well-defined platform to support functional components for molecular electronic applications.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The financial support by the Czech Science Foundation (18-14990S, 18-04682S), Czech Academy of Sciences (MTA-16-02, RVO: 61388955), Hungarian Academy of Sciences OTKA (NN 128168), Baden-Württemberg Stiftung (Functional Nano-structures) and the Helmholtz Research Program (Science and Technology of Nanosystems, "STN") is acknowledged.

## Notes and references

- 1 M. Valářek, M. Lindner and M. Mayor, *Beilstein J. Nanotechnol.*, 2016, 7, 374.
- 2 M. Valářek and M. Mayor, *Chem. – Eur. J.*, 2017, 23, 13538.
- 3 Z. Wei, X. Wang, A. Borges, M. Santella, T. Li, J. K. Sørensen, M. Vanin, W. Hu, Y. Liu, J. Ulstrup,

- G. C. Solomon, Q. Chi, T. Bjørnholm, K. Nørgaard and B. W. Laursen, *Langmuir*, 2014, **30**, 14868.
- 4 N. Hauptmann, L. Gross, K. Buchmann, K. Scheil, C. Schütt, F. L. Otte, R. Herges, C. Herrmann and R. Berndt, *New J. Phys.*, 2015, **17**, 013012.
- 5 S. Lemke, S. Ulrich, F. Claussen, A. Bloedorn, U. Jung, R. Herges and O. M. Magnussen, *Surf. Sci.*, 2015, **632**, 71.
- 6 S. Kuhn, U. Jung, S. Ulrich, R. Herges and O. Magnussen, *Chem. Commun.*, 2011, **47**, 8880.
- 7 B. Singhana, A. C. Jamison, J. Hoang and T. R. Lee, *Langmuir*, 2013, **29**, 14108.
- 8 S. Katano, Y. Kim, T. Kitagawa and M. Kawai, *Phys. Chem. Chem. Phys.*, 2013, **15**, 14229.
- 9 T. Kitagawa, Y. Idomoto, H. Matsubara, D. Hobara, T. Kakiuchi, T. Okazaki and K. Komatsu, *J. Org. Chem.*, 2006, **71**, 1362.
- 10 T. Kitagawa, H. Matsubara, K. Komatsu, K. Hirai, T. Okazaki and T. Hase, *Langmuir*, 2013, **29**, 4275.
- 11 S. U. Lee, H. Mizuseki and Y. Kawazoe, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11763.
- 12 K. Scheil, T. G. Gopakumar, J. Bahrenburg, F. Temps, R. J. Maurer, K. Reuter and R. Berndt, *J. Phys. Chem. Lett.*, 2016, **7**, 2080.
- 13 M. Valášek, K. Edelmann, L. Gerhard, O. Fuhr, M. Lukas and M. Mayor, *J. Org. Chem.*, 2014, **79**, 7342.
- 14 M. A. Karimi, S. G. Bahoosh, M. Valášek, M. Bürkle, M. Mayor, F. Pauly and E. Scheer, *Nanoscale*, 2016, **8**, 10582.
- 15 J. Šebera, V. Kolivoška, M. Valášek, J. Gasior, R. Sokolová, G. Mészáros, W. Hong, M. Mayor and M. Hromadová, *J. Phys. Chem. C*, 2017, **121**, 12885.
- 16 L. Gerhard, K. Edelmann, J. Homberg, M. Valášek, S. G. Bahoosh, M. Lukas, F. Pauly, M. Mayor and W. Wulfhekel, *Nat. Commun.*, 2017, **8**, 14672.
- 17 M. Lindner, M. Valášek, M. Mayor, T. Frauhammer, W. Wulfhekel and L. Gerhard, *Angew. Chem., Int. Ed.*, 2017, **56**, 8290.
- 18 M. Lindner, M. Valášek, J. Homberg, K. Edelmann, L. Gerhard, W. Wulfhekel, O. Fuhr, T. Wächter, M. Zharnikov, V. Kolivoška, L. Pospíšil, G. Mészáros, M. Hromadová and M. Mayor, *Chem. – Eur. J.*, 2016, **22**, 13218.
- 19 Y. Ie, T. Hirose, H. Nakamura, M. Kiguchi, N. Takagi, M. Kawai and Y. Aso, *J. Am. Chem. Soc.*, 2011, **133**, 3014.
- 20 Y. Ie, K. Tanaka, A. Tashiro, S. K. Lee, H. R. Testai, R. Yamada, H. Tada and Y. Aso, *J. Phys. Chem. Lett.*, 2015, **6**, 3754.
- 21 T. Sebechlebská, J. Šebera, V. Kolivoška, M. Lindner, J. Gasior, G. Mészáros, M. Valášek, M. Mayor and M. Hromadová, *Electrochim. Acta*, 2017, **258**, 1191.
- 22 V. Kolivoška, J. Šebera, T. Sebechlebská, M. Lindner, J. Gasior, G. Mészáros, M. Mayor, M. Valášek and M. Hromadová, *Chem. Commun.*, 2019, **55**, 3351.
- 23 S. Ramachandra, K. C. Schuermann, F. Edefe, P. Belser, Ch. A. Nijhuis, W. F. Reus, G. M. Whitesides and L. De Cola, *Inorg. Chem.*, 2011, **50**, 1581.
- 24 R. Sakamoto, Y. Ohirabaru, R. Matsuoka, H. Maeda, S. Katagiri and H. Nishihara, *Chem. Commun.*, 2013, **49**, 7108.
- 25 B. Xu and N. J. Tao, *Science*, 2003, **301**, 1221.
- 26 Y. Xing, T.-H. Park, R. Venkatramani, S. Keinan, D. N. Beratan, M. J. Therien and E. Borguet, *J. Am. Chem. Soc.*, 2010, **132**, 7946.
- 27 A. V. Tivanski, Y. He, E. Borguet, H. Liu, G. C. Walker and D. H. Waldeck, *J. Phys. Chem. B*, 2005, **109**, 5398.
- 28 M. Kiguchi, Y. Takahashi, S. Fujii, M. Takase, T. Narita, M. Iyoda, M. Horikawa, Y. Naitoh and H. Nakamura, *J. Phys. Chem. C*, 2014, **118**, 5275.
- 29 H. Vazquez, R. Skouta, S. Schneebeli, M. Kamenetska, R. Breslow, L. Venkataraman and M. S. Hybertsen, *Nat. Nanotechnol.*, 2012, **7**, 663.
- 30 C. Seth, V. Kaliginedi, S. Suravarapu, D. Reber, W. Hong, T. Wandlowski, F. Lafolet, P. Broekmann, G. Royal and R. Venkatramani, *Chem. Sci.*, 2017, **8**, 1576.
- 31 T. Hansen and G. C. Solomon, *J. Phys. Chem. C*, 2016, **120**, 6295.
- 32 M. Magoga and C. Joachim, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 16011.
- 33 J. Šebera, T. Sebechlebská, Š. Nováková Lachmanová, J. Gasior, P. Moreno Garcia, G. Mészáros, M. Valášek, V. Kolivoška and M. Hromadová, *Electrochim. Acta*, 2019, **301**, 267.
- 34 L. Rincon-Garcia, C. Evangeli, G. Rubio-Bollinger and N. Agrait, *Chem. Soc. Rev.*, 2016, **45**, 4285.
- 35 Š. Nováková Lachmanová, J. Šebera, V. Kolivoška, J. Gasior, G. Mészáros, G. Dupeyre, P. P. Lainé and M. Hromadová, *Electrochim. Acta*, 2018, **264**, 301.
- 36 J. C. Cuevas and E. Scheer, *Molecular Electronics: An Introduction to Theory and Experiment*, World Scientific, New Jersey, USA, 2010.
- 37 M. Di Ventra, *Electrical Transport in Nanoscale Systems*, Cambridge University Press, Cambridge, UK, 2008.
- 38 S. C. Veenstra, U. Stalmach, V. V. Krasnikov, G. Hadziioannou, H. T. Jonkman, A. Heeres and G. A. Sawatzky, *Appl. Phys. Lett.*, 2000, **76**, 2253.
- 39 N. Agrait, J. G. Rodrigo and S. Vieira, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 12345.
- 40 P. Moreno-García, M. Gulcur, D. Z. Manrique, T. Pope, W. Hong, V. Kaliginedi, C. Huang, A. S. Batsanov, M. R. Bryce, C. Lambert and T. Wandlowski, *J. Am. Chem. Soc.*, 2013, **135**, 12228.
- 41 V. Kaliginedi, A. V. Rudnev, P. Moreno-Garcia, M. Baghernejad, C. Huang, W. Hong and T. Wandlowski, *Phys. Chem. Chem. Phys.*, 2014, **16**, 23529.
- 42 M. Kiguchi, H. Nakamura, Y. Takahashi, T. Takahashi and T. Ohto, *J. Phys. Chem. C*, 2010, **114**, 22254.
- 43 T. Markussen, R. Stadler and K. S. Thygesen, *Nano Lett.*, 2010, **10**, 4260.