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Single-molecule conductance in a unique cross-conjugated tetra(aminoaryl)ethene†

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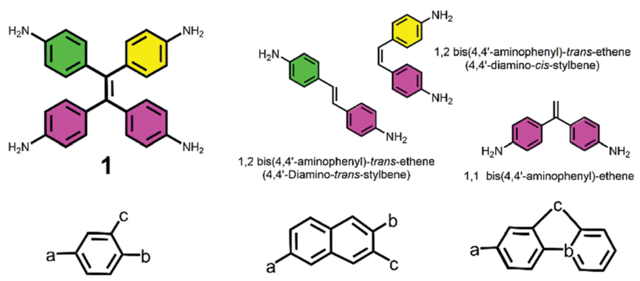
A 1,1,2,2-tetrakis(4-aminophenyl)ethene with three paths of π-conjugation, linear-*cis*, linear-*trans* and a cross-conjugation, has been prepared. The molecule is able to bind to gold electrodes forming molecular junctions for single-molecule conductance measurements. Only two regimes of conduction are found experimentally. The modelling of the conductance allows to assign them to through-bond transmission in the linear case, while the cross-conjugated channel is further assisted by through-space transmission, partially alleviating the destructive quantum interference

The combination of several forms of conjugation in π-conjugated systems confers greater versatility and multifunctionality to molecules, particularly in regard to their responses to external optical/electrical/chemical stimuli.[1,2] These conjugation forms should be preferably "orthogonal" in the sense that they might provide complementary responses, not interfering with each other. It is well known that, for the same number of π electrons, cross-conjugation[3,4] restricts π-electron delocalization compared to linear π-conjugation due to the alteration of the topology and connectivity pattern among the π-conjugated atoms. Furthermore, when dealing with linear π-conjugation, we can additionally refer to several cases, such as to linear conjugated pathways either with *cis*- or *trans*-configurations.[5] Our objective here is to study molecules with the simultaneous presence of linear- and cross-conjugation in order to assess if a palette of commutable electronic responses emerges.

Recently, the abilities of cross-conjugated molecules have been explored in several areas, such as: (i) molecular conductance devices;[6] (ii) electron-transfer responses by studying the influence on their mixed-valence properties;[7] (iii) diradicaloid molecules related with the tuning of the exchange coupling by cross-conjugation;[8] and (iv) photonic analysis regarding the extent of the changes in the absorption/emission properties. As for the later, an interesting phenomenon is aggregation induced emission (AIE),[9] and prototypical molecules disclosing AIE have been constructed based on tetraphenyl-substituted ethene (TPE).[10]

TPE contains several distinctive π-conjugation channels through the central vinylene bond among its four substituting arms. Considering the π-conjugation diversity of TPE, one can envision newer molecular derivatives of TPE that could potentially enhance the list of complementary features and versatility in terms of stimuli-responsive systems. In this paper, we have prepared and characterized 1,1,2,2-tetrakis(4-aminophenyl)ethene, **1**, a molecule in which the linear *cis*- and *trans*-π-conjugations and cross-π-conjugation coexist, as shown in Scheme 1. In addition, the other two molecules with only mono-conjugation, either with *trans*- and cross-conjugation have been prepared.[5] These latter mono-conjugated molecules will serve as a reference in the comparative studies with **1**.

In this article, the impact of the competition between linear- and cross-conjugations on the electronic properties of **1** is carefully investigated with a two-fold objective: (i) measuring



Scheme 1 Top: 1,1,2,2-Tetrakis(4-aminophenyl)ethene (**1**) and its parent models with only one form of conjugation. Bottom: Typical benzo-, naphto- and fluoreno-building blocks having linear-(through the a and b) and cross-conjugation (through the a–c) paths.

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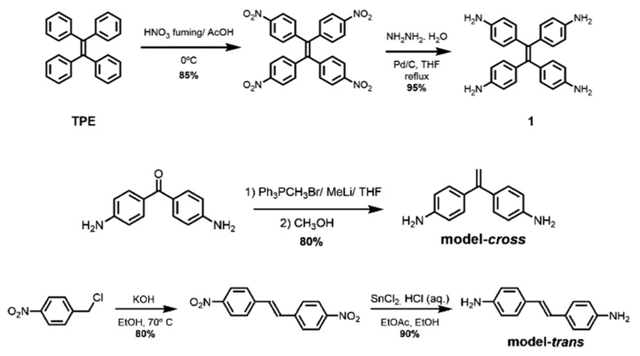
the conductance of junctions formed with **1** using the scanning tunnelling microscope-based break-junction (STM-BJ) method; and (ii) providing theoretical support for the underlying conduction mechanisms. In comparison to other molecules with both linear- and cross-conjugation paths, such as *meta*-benzo, naphto or fluoreno based systems (Scheme 1), **1** is the simplest case with two conjugation modes in competitive interaction through a common ethylene moiety (instead of the majority of cases through an aryl group).

The target molecule **1** has been synthesized following a reported procedure from commercially available TPE (Scheme 2).[11] The other derivatives were (Scheme 2) as previously reported.[12] See Schemes S1–S3 and Fig. S1–S5 in the ESI,† for further details.

The presence of amino groups allows for several sites of protonation. Titration of **1** with trifluoroacetic acid (TFA) has been found to be effective giving way to the formation of the diprotonated species in several configurations, either *cis*-, *trans*- or cross-dications (see Fig. S6–S9 and Table S1 (ESI†) for the titration and TD-DFT results). In this regard, the relative stability of the three bis-protonated forms of **1** has been explored using quantum chemical calculations (Fig. S10 and Tables S2–S4, ESI†).

For these dications, the linear *trans*-conjugated isomer is slightly the most stable, which is in agreement with the formation of a bis-protonated dication with the charges placed along the linear *trans*-conjugated pathway, likely due to the largest inter-charge distance. Calculations also predict that the next most stable species is the cross-conjugated bis-protonated dication at +0.27 kcal mol^{-1} from the *trans*-conjugated form; and finally, the linear *cis*-conjugated isomer with an energy difference of +1.79 kcal mol^{-1} relative to the *trans*-dication. From the optimized geometries in the bis-protonated forms of **1** (Fig. 1), we obtained an estimate of the three N^+–N^+ distances involved to be 0.80 nm, 1.23 nm, and 0.97 nm for the linear *cis*-conjugated, linear *trans*-conjugated and cross-conjugated bis-protonated isomers, respectively.

In the same way **1** undergoes acid–base reaction, the presence of primary amines in **1** affords the ability to coordinate to metals such as gold. Conveniently, this allows the formation of metal–molecule junctions in which single molecule conductance measurements can be carried out (see the ESI,† for details).[13]



Scheme 2 Synthetic route to **1** and its model compounds with only one form of conjugation.

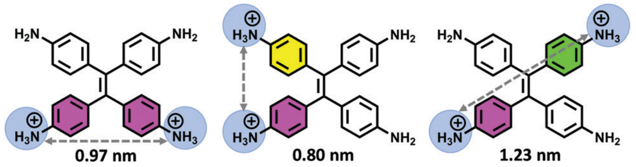


Fig. 1 Theoretical distances of the bis-protonated forms of **1** in the cross- (left), *cis*- (middle) and *trans*-conjugated (right) dispositions.

Compound **1** can bind to the junction in either a *cis*-, *trans*- or cross-conjugated geometry. Using the STM-BJ technique, we measured the single-molecule conductance of **1** in propylene carbonate at 100 mV bias. We observed two distinct peaks for **1** (Fig. 2a) – a high conductance feature with a peak conductance of 5 × 10^{-4} G_0 and a low conductance feature with a peak conductance of 1.3 × 10^{-5} G_0. Since cross-conjugated compounds are known to exhibit lower conductances,[14] we attribute the lower value to the cross-conjugated geometry, while the high conductance feature should account for both the *cis*- and *trans*-geometries which is supported by the similar conductance values reported for known linearly conjugated stilbenes.[15] STM-BJ measurements with the model-cross and model-*trans*, were also performed and the results are shown in Fig. 2. For the model-cross compound, the main conductance peak is at 5.8 × 10^{-5} G_0, while for the model-*trans* the peak conductance is at 9.4 × 10^{-4} G_0. These values are close but not the same as those measured with **1**. Model-*trans* has a higher conductance than that of the high-conductance peak of **1** and model-cross has a higher conductance than that of the low-conductance of **1**.

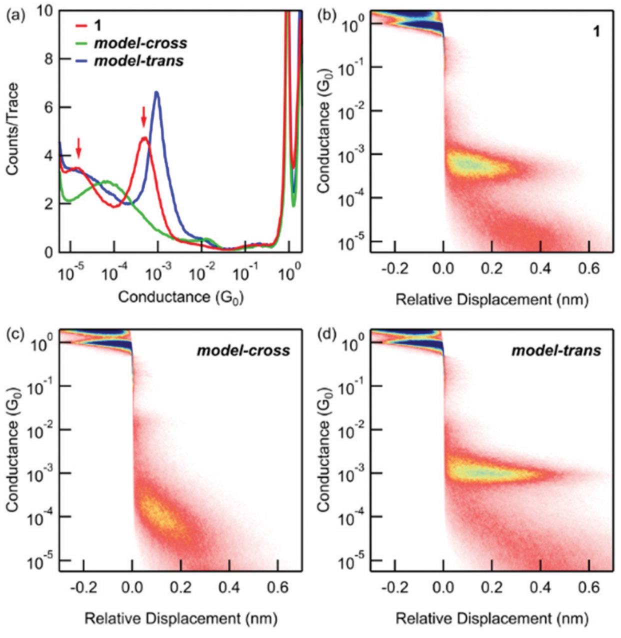


Fig. 2 (a) 1D conductance histogram compiled from 10 000 traces at 100 mV bias for the three compounds of **1**. Arrows indicate the peak positions of **1**; (b–d) 2D conductance histograms compiled from 10 000 traces at 100 mV bias. Conductance values are calculated from the peak positions in the 1D histograms.

In Fig. 2b–d, we present the 2D histogram of the data given in Fig. 2a. We observe a conductance plateau length of ~0.4–0.5 nm for both the low and high conductance features of **1**. From the optimized geometries of the bisprotonated forms of **1** (Fig. 1), the N–N distances were estimated to be 0.80 nm, 1.23 nm, and 0.97 nm for the *cis*-, *trans*-, and cross-conjugated isomers, respectively. The experimentally observed plateau lengths are consistent with these since the plateau length will always be an underestimate of the true molecule length.[16] Interestingly, from the 2D histograms in Fig. 2c and d, of the model-cross and model-*trans* compounds, we observe different conductance plateau lengths of ~0.3 and ~0.5 nm, respectively, conversely to **1** in which these are roughly similar.

To gain further insight into the nature of the lower conductance in the cross-conjugated disposition of **1**, we have evaluated the transmission spectra and local current maps for the three plausible contact geometries (*cis*-, *trans*- and cross-), using DFT combined with the non-equilibrium Green's function (NEGF) method (see the ESI,† for further details).[17] Amine–gold molecular junctions were modelled according to the geometrical characteristics provided by Venkataraman *et al.*,[18] and the known fact that conductance is relatively insensitive to the amino–gold junction geometry.[19,20] From the transmission functions shown in Fig. 3 (Fig. S11–S13, ESI,† for additional details), the three species of **1** display transmission maxima peaks (dotted red lines) at: (i) $E - E_F \simeq -0.6$ eV, which can be assigned to resonant transmission through the HOMO orbitals (theoretical values of the HOMO for the bisprotonated dications are at $-0.3/-0.4$ eV from the $E_F = -5.1$ eV of gold, see Fig. S10 and Table S4, ESI†); and (ii) $E - E_F \approx +3.0$ eV, which is ascribed to transmission through the LUMOs (theoretical values at +2.9/+3.0 eV relative to the $E_F = -5.1$ eV of gold).

The linear contact configurations, either *cis*- or *trans*-, exhibit very similar conductance related with the fact that in the STM-BJ experiments peaks ascribed to these two anchoring modes could not be distinguished. Also, the cross-anchoring configuration displays reduced transmission values that can be ascribed to a quantum interference which defines a transmission minimum between the HOMO and LUMO peaks. Accordingly, the experimentally measured low-conductance state corresponds to the cross-conjugated connection,[21,22] whereas the high-conductance state can be assigned to the linear-conjugated one. At the Fermi level, the linear conjugated junctions exhibit around two-fold enhancement as compared to the cross-conjugated case, in line with the conductance ratios measured experimentally.

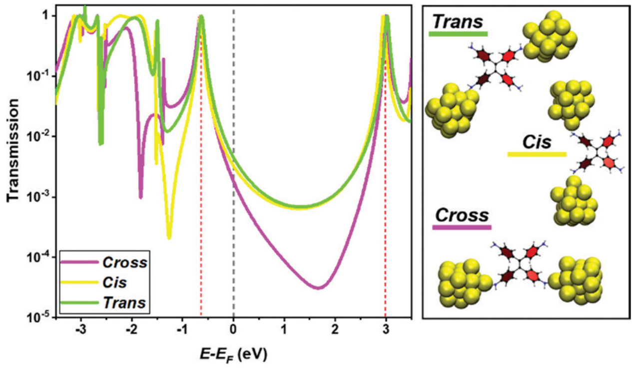


Fig. 3 Theoretically predicted transmission spectra for **1** in its three cross-, *cis*- and *trans*-anchoring configurations on Au_{19} clusters.

Furthermore, calculations for the model-*cis* and model-*trans* compounds predict rather different (Fig. S14, ESI†). In general, the values predicted for the model-compounds are slightly higher than those of the analogue conformations of **1**, which is in line with the tendencies detected experimentally. The plausible explanations for these differences in the conductance values between **1** and its model molecules are the increasing distortion between the arms of **1** and also the electron donor mesomeric effect of the substitution on the central ethylene, which is absent in the model compounds.

The above comparison reveals that cross-conjugation in model-cross and in the cross-disposition of **1** does not provoke conduction blockade. These results are in accordance with recent studies in *meta* cross-conjugated fluorenones.[23] In common with these fluorenones, **1** has the feature that its cross-conjugated disposition does not show a sharp minimum of conductance around the Fermi level in the HOMO–LUMO gap but a rather smooth decrease with a shallow minimum revealing the alleviation of the destructive quantum interference. Conversely to the fluorenones, **1** is a unique example in which linear- and cross-conjugations are formally competing through the same path (ethylene group). Notice here that in *meta*-fluorenones the cross- and linear-conjugated paths do not reside in the same set of atoms (see Fig. S15, ESI†).

From the local current maps at the Fermi level[20] shown in Fig. 4 and Fig. S16 (ESI†), we can visualize the differences in the current flow through **1** as a function of the anchoring configurations. Whereas the current flows through the central C=C bond in *cis*- and *trans*-configurations, the main transmission pathway in the cross-conjugated disposition partially avoids the central double bond. For this, there is a complementary transmission circuit which apparently consists of a through-space channel between non-connected atoms, as shown in Fig. 4. In the frontier molecular orbitals of the cross-disposition of **1**, we found: (i) the HOMO largely spreads over the cross-path, and (ii) the LUMO contains a through space path which might be responsible for that predicted in the local current map. These

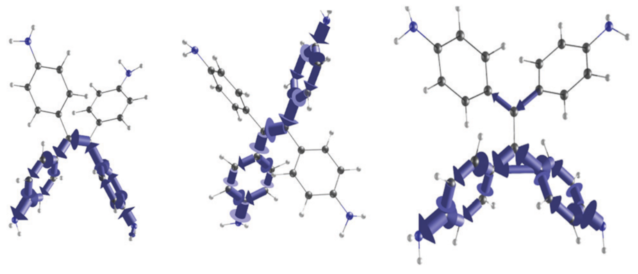


Fig. 4 Local transmission plots at the Fermi level for the *cis*-linear, *trans*-linear and cross-conjugation configuration of **1**.

two effects might alleviate the opposite effect of the destructive interference producing the experimental detection of molecular conductance over the crossed path.

These findings reveal that at the initial detraction distances in the STM-BJ experiment, a larger conductance peak is measured which should be adhered to conduction channels between the two forms of linear conjugation. However, given the smaller N–N distance of the *cis*-anchoring mode, it could better fit the junction volume at the initial stages of the measure thus likely displaying the dominant contribution. Enlargement of the junction distance leaves only the cross-conjugation channel active which is the species with the next largest N–N distance. This description in terms of space filling factors is feasible owing to the similar energetics of the three structures, which are accessible under experimental conditions (see discussion above).

In summary, a tetrakis-(1,4-aminophenyl)ethene has been synthesized in which two main π-conjugation pathways exist, a linear-one (with *cis*- and *trans*-connectivity) and a cross-conjugated one. Two model compounds with only *trans*- and cross-conjugations have been also prepared and studied. The presence of amino anchoring groups allows them to be sandwiched in the break gold heterojunctions for single-molecule conductance in a scanning tunnelling microscope. Despite **1** having three possible connections, we detect two main regimes of conduction: a high conductance value corresponding to the contribution of the linear-connections and a low conductance value ascribed to the cross-conjugation channel. Quantum chemical modelling for the three geometries of **1** and for the model compounds reproduces the experimental values. The through-bond connection in the cross-conjugation channel produces destructive quantum interference, which is partially alleviated by an alternative through-space transmission channel. **1** represents one of the simplest cases of cross-conjugation conductance in which the competition with linear-conjugation occurs through the common ethylene, a distinctive feature regarding other aryl-based molecular wires exhibiting linear- and cross-conjugations.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 IUPAC Compendium of Chemical Terminology, in *The Gold Book*, ed. A. D. McNaught and A. Wilkinson, PAC, 2nd edn, 1994, vol. 66, p. 1077.
2 R. Hoffmann, C. Janiak and C. A. Kollmar, *Macromolecules*, 1991, **24**, 3725.
3 (*a*) N. F. Phelan and M. Orchin, *J. Chem. Educ.*, 1968, **45**, 633; (*b*) M. Gholami and R. R. Tykwinski, *Chem. Rev.*, 2006, **106**, 4997; (*c*) M. B. Nielse and F. Diederich, *Chem. Rev.*, 2005, **105**, 1837.
4 R. Emanuelsson, A. Wallner, E. A. M. Ng, J. R. Smith, D. Nauroozi, S. Ott and H. Ottosson, *Angew. Chem., Int. Ed.*, 2013, **52**, 983.
5 D. L. Beveridge and H. H. Jaffe, *J. Am. Chem. Soc.*, 1965, **87**, 5340.
6 (*a*) G. C. Solomon, D. Q. Andrews, R. H. Goldsmith, T. Hansen, M. R. Wasielewski, R. P. V. Duyne and M. A. Ratner, *J. Am. Chem. Soc.*, 2008, **130**, 17301; (*b*) J. Gu, W. Wu, T. Stuyver, D. Danovich, R. Hoffmann, Y. Tsuji and S. Shaik, *J. Am. Chem. Soc.*, 2019, **41**, 6030.
7 E. Göransson, R. Emanuelsson, K. Jorner, T. F. Markle, L. Hammarström and H. Ottosson, *Chem. Sci.*, 2013, **4**, 3522.
8 (*a*) D. S. Shultz, R. M. Fico, S. H. Bodnar, R. K. Kumar, K. E. Vostrikoba, J. W. Kampf and P. D. Boyle, *J. Am. Chem. Soc.*, 2003, **125**, 11761; (*b*) C. Zhang, S. M. Rivero, W. Liu, D. Casanova, X. Zhu and J. Casado, *Angew. Chem., Int. Ed.*, 2019, **58**, 11291.
9 X. Yan, H. Wang, C. E. Hauke, T. R. Cook, M. Wang, M. L. Saha, Z. Zhou, M. Zhang, X. Li, F. Huang and P. J. Stang, *J. Am. Chem. Soc.*, 2015, **137**, 15276.
10 J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718.
11 Y. Lin, X. Jiang, S. T. Kim, S. B. Alahakoon, X. Hou, Z. Zhang, C. M. Thompson, R. A. Smaldone and C. Ke, *J. Am. Chem. Soc.*, 2017, **139**, 7172.
12 (*a*) X. Liu, H. Liu, W. Zhou, H. Zheng, X. Yin, Y. Li, Y. Guo, M. Zhu, C. Ouyang, D. Zhu and A. Xia, *Langmuir*, 2010, **26**, 3179; (*b*) G. J. Summers, M. P. Ndawuni and C. A. Summers, *Polym. Int.*, 2014, **63**, 876.
13 B. Xu and N. J. Tao, *Science*, 2003, **301**, 1221.
14 T. A. Su, M. Neupane, M. L. Steigerwald, L. Venkataraman and C. Nuckolls, *Nat. Rev. Mater.*, 2016, **1**, 16002.
15 S. V. Aradhya, J. S. Meisner, M. Krikorian, S. Ahn, R. Parameswaran, M. L. Steigerwald, C. Nuckolls and L. Venkataraman, *Nano Lett.*, 2012, **12**, 1643.
16 M. Kamenetska, M. Koentopp, A. C. Whalley, Y. S. Park, M. L. Steigerwald, C. Nuckolls, M. S. Hybertsen and L. Venkataraman, *Phys. Rev. Lett.*, 2009, **102**, 126803.
17 C. Herrmann, G. C. Solomon, J. E. Subotnik, V. Mujica and M. A. Ratner, *J. Chem. Phys.*, 2010, **132**, 024103.
18 S. Y. Quek, L. Venkataraman, H. J. Choi, S. G. Louie, M. S. Hybertsen and J. B. Neaton, *Nano Lett.*, 2007, **7**, 3477.
19 S. Y. Quek, H. J. Choi, S. G. Louie and J. B. Neaton, *ACS Nano*, 2011, **5**, 551.
20 L. Venkataraman, J. E. Klare, I. W. Tam, C. Nuckolls, M. S. Hybertsen and M. L. Steigerwald, *Nano Lett.*, 2006, **6**, 458.
21 H. Valkenier, C. M. Guédon, T. Markussen, K. S. Thygesen, S. J. van der Molen and J. C. Hummelen, *Phys. Chem. Chem. Phys.*, 2014, **16**, 653.
22 G. C. Solomon, C. Herrmann, T. Hansen, V. Mujica and M. A. Ratner, *Nat. Chem.*, 2010, **2**, 223.
23 A. Alanazy, E. Leary, T. Kobatake, S. Sangtarash, M. T. González, H.-W. Jiang, G. Rubio Bollinger, N. Agräit, H. Sadeghi, I. Grace, S. J. Higgins, H. L. Anderson, R. J. Nichols and C. J. Lambert, *Nanoscale*, 2019, **11**, 13720.