

## Camouflaged Holes Assist Negative Charge Motion in Radical-Anion Molecular Wires

**Paula Mayorga Burrezo<sup>a</sup>, Carlos Franco<sup>b</sup>, Vega Lloveras<sup>b</sup>, Rubén Caballero<sup>c</sup>, Isaac Alcón<sup>d</sup>, Stefan Bromley<sup>\*,d,e</sup>, Marta Mas-Torrent<sup>b</sup>, Fernando Langa<sup>c</sup>, Juan T. López Navarrete<sup>a</sup>, Concepció Rovira<sup>\*,b</sup>, Juan Casado<sup>\*,a</sup>, Jaime Veciana<sup>\*,b</sup>**

*a, Department of Physical Chemistry, University of Malaga, Campus de Teatinos s/n, 29071 Malaga, Spain.*

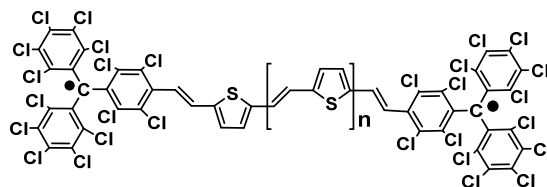
*b, Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari de Bellaterra, E-08193, Cerdanyola, Barcelona, Spain.*

*c, Instituto de Nanociencia, Nanotecnología y Materiales Moleculares (INAMOL), University of Castilla-La Mancha, Campus de la Fábrica de Armas, 45072 Toledo, Spain.*

*d, Institute of Theoretical and Computational Chemistry (IQTIC) & Department of Materials Science and Physical Chemistry, Faculty of Chemistry, University of Barcelona, 08028-Barcelona, Spain*

*e, Catalan Institution of Research and Advanced Studies (ICREA), 08010-Barcelona Spain*

Charge transfer in molecular wires over varying distances is a subject of great interest in the field of molecular electronics. By increasing the distance between the electroactive centers, transport mechanisms generally accounted for on the basis of tunneling or superexchange operating over small distances, progressively gives way to hopping assisted transport. However, the underlying molecular sequential steps that likely take place during hopping and the operative mechanism occurring at intermediate distances have received much less attention given the difficulty in assessing detailed molecular-level information. We describe here the operating mechanisms for unimolecular electron transfer in the ground state of radical-anion mixed-valence derivatives occurring between their terminal perchlorotriphenylmethyl/ide groups through thiophene-vinylene oligomers that act as conjugated wires of increasing length up to 30 Å. In this sense, while in the shorter radical-anions a flickering resonance mechanism is the operative one, in the larger molecular wires, as a unique finding, the net transport of the electron is assisted by an electron-hole delocalization.



**Figure 1. Chemical structure of •PTM-nTV-PTM• oligomers (n = 1-6)**