

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

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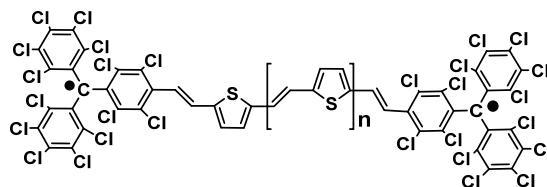
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Charge transfer in molecular wires over varying distances is a subject of great interest in the field of molecular electronics. By increasing the distance between the electroactive centers, transport mechanisms generally accounted for on the basis 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)**