Molecular Wires

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Putting a Positive Spin on Molecular Bridges**

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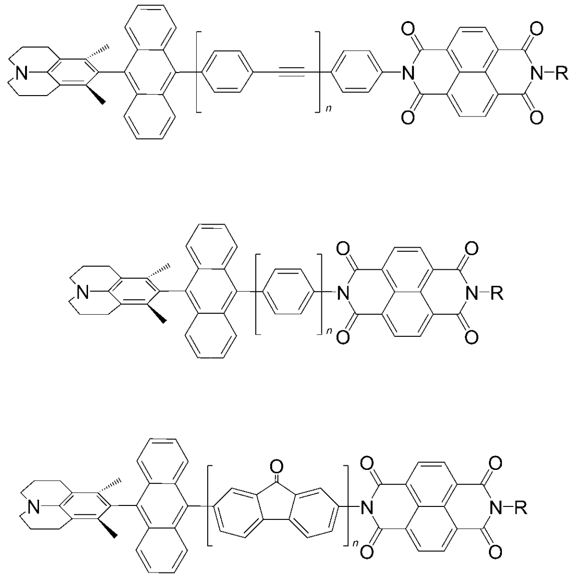
charge transfer · electron acceptors · molecular wires · spin

Dedicated to Professor David I. Schuster on the occasion of his 75th birthday

One of the major themes in electronics is the construction, measurement, and understanding of the current/voltage response of an electronic circuit, in which molecular conjugates act as conducting elements.[1] In this regard, electron-donor/acceptor architectures have emerged as suitable models for probing charge-transfer processes at the molecular level. Molecular bridges—which connect electron donors and electron acceptors—are assumed to mediate charges between the donor and acceptor termini. To this end, the study by Wasielewski and co-workers[2] constitutes a real breakthrough in the field of molecular conjugates. In particular, their outstanding study of a series of electron donor/acceptor conjugates (Scheme 1) by means of magnetic field dependence comprehensively sheds light onto singlet and triplet charge recombination pathways.

Desirable features that render molecular building blocks, namely, donor, bridge, and acceptor, suitable candidates for electronic components are as follows:[3] 1) structural tunability, which can be achieved by a large number of synthetic methods, allows greater control and more flexibility than is given by metallic and semimetallic conductors; 2) an energetic gradient between the molecular orbitals that permits unidirectional movement of charge carriers within the molecule; and 3) a predisposed distribution of electron density in the molecules that determines whether charge transport occurs with spin preservation or with a change in the spin state.

Intrinsically, charge transfer is a non-adiabatic process. Its rate is determined by a combination of strongly distance-dependent tunneling and weakly distance-dependent incoherent transport events.[4,5] Tunneling occurs by a superexchange mechanism, where charges are transferred from the donor to the acceptor through an energetically isolated bridge.[6,7] On the other hand, incoherent or sequential charge transfer involves real intermediate states that couple to internal nuclear motions of the molecular bridge and the surrounding medium. This mechanism is defined as thermally activated incoherent hopping.[8,9] The attenuation factor β is used to describe the quality of the molecular bridge, since it describes the decay of the charge-transfer rate constant k as a function of distance r_{DA}.[10] The attenuation factor β is also used to determine whether electron-donor/acceptor architectures should be considered as having the ability to function as molecular wires. Thus, β quantifies the charge-transfer capability of the molecular bridge and, therefore, becomes a bridge-specific parameter, which depends on the magnitude of the coupling between the donors and acceptors as well as the energy of the charge-transfer states localized on each site. Equally importantly, the connectivity between the donor, bridge, and acceptor has a high impact on the charge-transfer rates. A small β value would allow charges to be transferred over larger distances. Importantly, such a definition of β only applies to exponentially decaying processes. In addition, the limit of a very small β describes band transport, a so-called "π-electron pathway" along which charges can travel coherently. Typical values for β range from 1.0 to 1.4 Å^{-1} for protein structures (Figure 1)[11] and from 0.01 to 0.04 Å^{-1} for highly π-conjugated bridges (Scheme 2).[12–19] In a vacuum, the values of β are relatively large, namely in the range of 2.0 to 5.0 Å^{-1}.[20] Moreover, several other parameters exert an impact on the rate of charge transfer.[21–24] These are, in



Scheme 1. Chemical structures of 3,5-dimethyl-4-(9-anthracenyl)julolidine/naphthalene-1,8:4,5-bis(dicarboximide) electron donor/acceptor conjugates linked by fluorenone (top), *p*-phenylethynylene (center), and *p*-phenylene (bottom) bridges.

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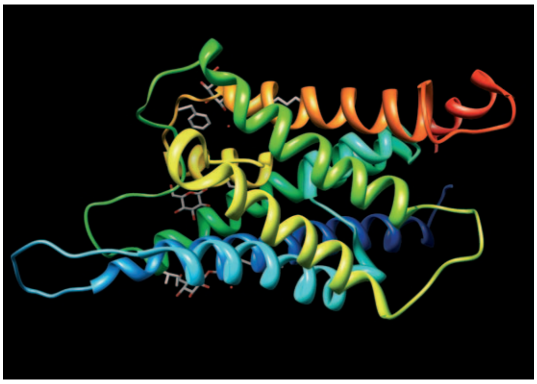
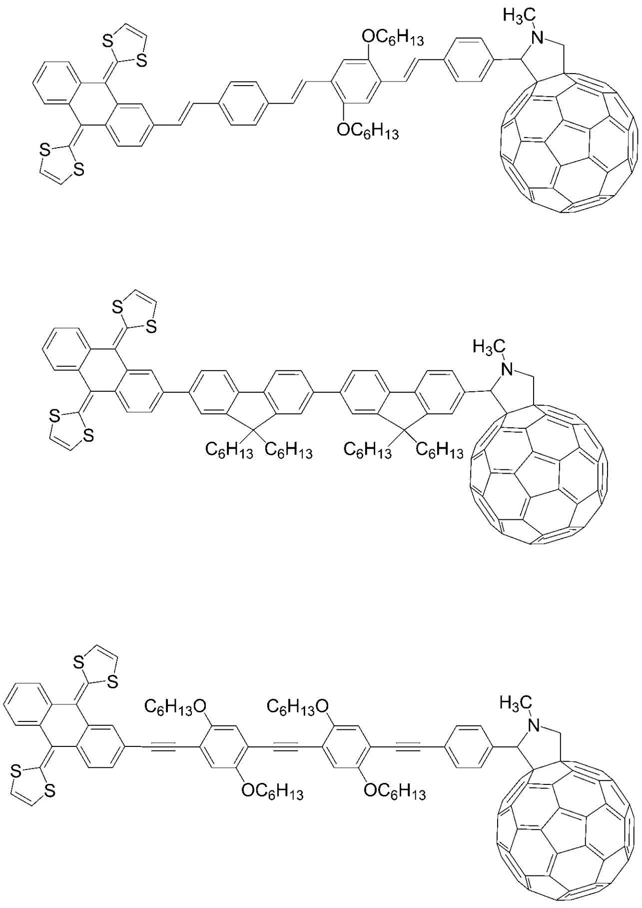


Figure 1. Example of a cell membrane protein: aquaporine.



Scheme 2. Chemical structures of leading π-extended tetrathiofulvalene (exTTF)/C_{60} electron donor/acceptor conjugates linked by oligo-*p*-phenylenevinylene (top), oligofluorene (center), and oligo-*p*-phenyleneethynylene (bottom) bridges.

particular, the underlying driving forces ($-\Delta G^{\circ}$), the corresponding reorganization energies (λ), and the electronic couplings (V) that exist between the electron donor and electron acceptor. In summary, the use of rigid electron donors and electron acceptors of various bridge lengths allows for the measurement of distance-dependent charge-transfer rates to elucidate how the superexchange and hopping charge-transfer regimes within molecular systems depend on structure.

The thrust of the study by Wasielewski and co-workers[2] was to incorporate components that exhibit molecular-wire behavior into electron donor/acceptor architectures to improve performance features—from the dynamics of charge separation and charge recombination to quantum yields of charge separation. In particular, a comparison of highly π-conjugated bridges consisting of fluorenones ($n=1$–3), *p*-phenylethynylene ($n=1$–3), and *p*-phenylene ($n=1$-5) that connected an electron donor—3,5-dimethyl-4-(9-anthracenyl)julolidine—with an electron acceptor—naphthalene-1,8:4,5-bis(dicarboximide)—stood at the forefront of their investigations (Scheme 1). These molecules play an important role in a number of important applications—electrical conductors, photovoltaic cells, electroluminescent devices, etc—where long-range charge-/energy-transfer processes constitute a common mode of operation. The most important conclusion from this study is that the value of β in these highly π-conjugated bridges is a function of the spin-selective charge-recombination pathways.

To be precise, the initially formed singlet radical ion pair undergoes electron-nuclear hyperfine coupling induced intersystem crossing to produce the triplet radical ion pair. It is fundamentally important that the subsequent charge recombination is spin selective, that is, the singlet radical ion pair recombines to give the singlet ground state, and the triplet radical ion pair recombines to yield the triplet excited state located on either 3,5-dimethyl-4-(9-anthracenyl)julolidine or naphthalene-1,8:4,5-bis(dicarboximide). By monitoring the yield of the local triplet production as a function of the applied magnetic field B, Wasielewski and co-workers measured the magnitude of the spin–spin exchange interactions ($2J$) to provide insights into electronic coupling (V). A kinetic analysis of the magnetic field effects was used to separate the rate constants for the spin-selective charge-recombination pathways. This enabled the authors to conclude that the triplet pathway is more efficient for the fluorenones and *p*-phenylethynylene bridges for spin-selective charge recombination, as is also the case for the longer bridge lengths in the *p*-phenylene series. In fact, the dependence of the two charge recombination pathways on the energy gap illustrates that contributions from the triplet pathway are located in the Marcus normal region, while those from the singlet pathway are in the inverted region. The β values for the fluorenones and *p*-phenylethynylene bridges are comparable in magnitude—a surprising finding that highlights the system dependence and not the bridge dependence.

It should be emphasized that such a systematic investigation of molecular wire behavior has, already at a relatively early stage, played a significant role in the development of useful molecular building blocks.[25,26] If the more technological problems can be solved, an almost unlimited field of application can be foreseen and molecular wires may eventually become important building blocks in emerging technologies. From a more visionary viewpoint, these nanoscale molecular building blocks may help minimize the dimensions of computer circuits and enhance performance.

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