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Fullerene for organic electronics†

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This tutorial review surveys and highlights the integration of different *molecular wires*—in combination with chromophores that exhibit (i) significant absorption cross section throughout the visible part of the solar spectrum and (ii) good electron donating power—into novel electron donor–acceptor conjugates. The focus is predominantly on charge transfer and charge transport features of the most promising systems.

1. Introduction

Donor–bridge–acceptor (DBA) architectures have emerged as suitable models for probing electron transfer processes at the molecular level. In such, the bridge is assumed to mediate charge transfer between the donor and the acceptor. One of the most striking scenarios implies wire-like behavior. In other words, electron transfer processes (*i.e.*, charge separation and charge recombination) depend either weakly on distance or

completely lack any dependence. In donor–acceptor conjugates, visible light excitation, for instance, may result in a charge transfer—mediated by the bridge—from the photoexcited donor to the acceptor or from the donor to the photoexcited acceptor. The kinetics of both processes, namely, charge separation and/or charge recombination are then reflected by the electron transfer rate constant:

$$k_{\text{ET}} = k_0 \exp(-\beta R_{\text{DA}})$$

where k_0 is a kinetic prefactor/preexponential factor, R_{DA} represents the donor–acceptor distance and β is the so-called attenuation factor or dumping factor. At first glance, β quantifies the charge transfer capability of the bridge and therefore becomes a bridge specific parameter, which depends on the magnitude of the coupling between the donor and acceptor sites and the energy of the electron (or hole) transfer states localized on each site. Equally important, the connectivity patterns between donor, bridge and acceptor highly impact the electron transfer rates. Overall, β has been implemented to assess wire-like behavior in a wide variety of

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† Dedicated to Professor Jean-Pierre Sauvage on the occasion of his 65th birthday.



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Beatriz M. Illescas obtained her degree in Chemistry at the Universidad Complutense of Madrid, in 1992, where she received her PhD degree in 1998 under the direction of Professors C. Seoane and N. Martín. In 1998 she worked as postdoctoral researcher on the synthesis of fullerenes with pharmaceutical activity, in a project with Janssen-Cilag S.A. Since 1999 she has been appointed as an assistant professor at the Universidad Complutense of

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donor–acceptor conjugates. Typical values for β range, on one hand, from 1.0 to 1.4 Å⁻¹ for protein structures and, on the other hand, from 0.01 to 0.04 Å⁻¹ for highly π -conjugated bridge structures.¹ In vacuum, values of β are relatively large in the range of 2.0 to 5.0 Å⁻¹. Moreover, several other parameters exert an impact on the electron transfer rate. These are in particular the underlying driving forces ($-\Delta G^\circ$), the corresponding reorganization energies (λ), and the electronic couplings that exist between electron donor and electron acceptor (V).

With the aforementioned in hand, we may address a series of basic requirements for the design of molecular systems that exhibit efficient wire-like behavior: (i) matching of energy levels (orbitals) between donor/acceptor and the bridge sites, (ii) strong electronic couplings between the electron donor and acceptor units *via* the bridge orbitals, and (iii) small attenuation factors.



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As a matter of fact, recent strategies have built on the incorporation of components that exhibit wire-like behavior into electron donor/acceptor structures to improve the overall performance features—ranging from charge separation/charge recombination dynamics to charge separation quantum yields. These molecules play an overriding role in a number of important applications—electrical conductors,^{2,3} photovoltaic cells,^{4,5} electroluminescent devices,^{6,7} nonlinear optics,⁸ and field-effect transistors.⁹ Therein, long-range electron/energy transfer processes constitute a common mode of operation. The thrust of this review is to survey, highlight and compare methods that are currently employed to probe molecular systems or fragments with respect to their capability to efficiently transport charges along the molecular framework from one site to another.

To this end, two different strategies have been implemented. The first of these is based on the covalent linkage of electron donors to electron acceptors by molecular wires. A certain degree of charge delocalization, that is, a transfer of charge density from the donor to the acceptor, may occur in the ground state. Nevertheless, we will focus on electron donor/acceptor structures, where irradiation with light induces the promotion of electrons from the donor to the acceptor to yield a spatially separated radical ion pair. For non-fullerene-containing conjugates, this topic has been extensively reviewed in literature.¹⁰ Thus, we will limit ourselves to the description of examples where fullerenes play an integrative role. The second strategy involves embedded fullerenes and fullerene derivatives between two electrodes. Applying an external potential to the electrodes leads to conductance along the molecular framework. It is important to note, however, that the presence of an electron donor unit linked to a fullerene moiety by a conjugated spacer does not necessarily guarantee the formation of a charge separated state. Instead, energy transduction or even competitive simultaneous or sequential energy and electron transfer processes may occur.



Mateusz Wielopolski

Mateusz Wielopolski was born in Katowice in Poland in 1981. He moved to Germany in the early 1990s, where he completed his education. In 2006, he received his Master of Science in Molecular Nano Science from the University of Erlangen (Master Thesis Award). He obtained his PhD two and a half years later in February 2009 at the University of Erlangen for his research on molecular wires.



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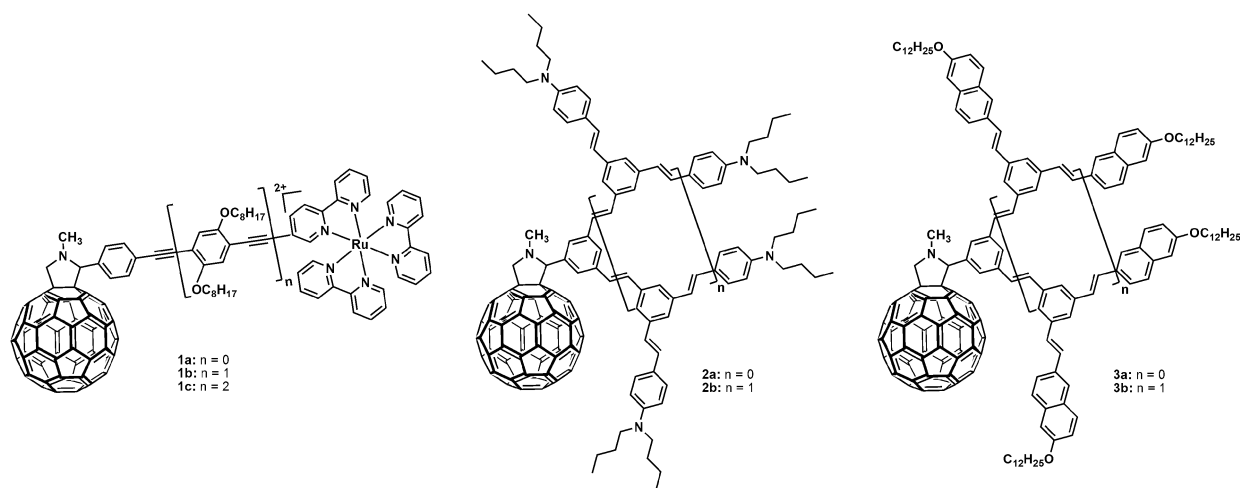


Fig. 1 Examples of D-oligomer- C_{60} (**1a-c**) and D-dendrimer- C_{60} (**2a,b** and **3a,b**) systems.

An intriguing example are phenyleneethynylene oligomers of varying length (**1a-c**) that connect a fullerene to a ruthenium trisbipyridine.¹¹ These oligomers show transduction of energy—starting with the excited ruthenium MLCT state, forming intermediately the $\pi-\pi^*$ state of the oligomer and relaying it to the fullerene—that is nearly distance independent (Fig. 1), even for edge-to-edge distances up to 2.3 nm. Overall, the experiments suggest an interesting alternative for long-range energy transfer in which excited-state energy is efficiently transferred *via* near-isoelectronic bridge states, which decrease in energy with increasing spacer, may mediate constant energy transfer rates.

To contrast the interplay between competitive energy and charge transfer processes, several phenylenevinylene-based dendrons bearing dibutylaniline (**2a,b**) or dodecyloxynaphthalene (**3a,b**) electron donors have been designed.^{12,13} Efficient and rapid energy transfer dominates the intramolecular deactivation of the excited dendrons, generating the fullerene singlet excited state in nearly quantitative yields. A spectroscopic and kinetic analysis, however, confirms the presence of an alternative intramolecular charge transfer reaction which yields the $C_{60}^{\bullet-}$ -dendron $^{\bullet+}$ radical ion pair state. It is the energy gap—the energetic positioning of the radical ion pair state relative to the singlet excited states of the dendron and fullerene—that controls the outcome, namely, either a sequential (**2a,b**) or a competitive (**3a,b**) scenario for the energy and charge transfer processes.

In summary, this review is aiming to demonstrate that utilizing the unique electronic features of fullerenes help to determine and to compare the β values of a variety of structurally different wire-like architectures, which are of particular interest for molecular electronics. Furthermore, it paves the way for the evaluation of molecular components (*i.e.* fullerene derivatives, molecular wires, *etc.*) with respect to their performance in molecular devices and molecular electronic circuits.

2. C_{60} -wire-donor systems

The molecular bridge which links the donor to the acceptor is considered to play a vital role in the light of several key

aspects.¹⁴⁻¹⁶ First, covalent linkers eliminate diffusion as the rate determining step of the charge transfer process. This helps to accelerate the electron transfer dynamics. Second, the chemical nature and the length of the bridge presides over the donor-acceptor separation, orientation, overlap and topology. Implicit here, a structurally rigid bridge prevents unrestrained and undesired rearrangements. Structural flexibility, on the other hand, may lead to different photo-reactivities (*i.e.*, reaction rates, pathways, products, *etc.*). Third, the chemical nature of the bridge (*e.g.* π -conjugation) strongly affects the conductance/charge-transport behavior. Finally, the influence of the bridge on the electronic nature of the donor/acceptor pair is supposed to be negligible, and the coupling of the bridge to the donor/acceptor sites is proportional to the overlap between their electronic clouds.

2.1 C_{60} -wire-ZnP systems

Fig. 2 illustrates a few leading examples, in which a ZnP donor and C_{60} are connected through diverse bridges. These comprise either (i) a $-\text{CO}-\text{NH}-$ amide bond (**4**) (in THF: $k_{\text{CS}} = 2.2 \times 10^{10} \text{ s}^{-1}$; $k_{\text{CR}} = 2.0 \times 10^6 \text{ s}^{-1}$), (ii) a $-\text{NH}-\text{CO}-$ reversed amide bond (**5**) (in THF: $k_{\text{CS}} = 1.7 \times 10^{10} \text{ s}^{-1}$; $k_{\text{CR}} = 3.7 \times 10^5 \text{ s}^{-1}$), (iii) a $-\text{C}\equiv\text{C}-$ triple bond (**6**) (in THF: $k_{\text{CS}} = 3.7 \times 10^{10} \text{ s}^{-1}$; $k_{\text{CR}} = 1.5 \times 10^6 \text{ s}^{-1}$) or (iv) a $-\text{N}=\text{N}-$ double bond (**7**) (in THF: $k_{\text{CS}} = 7.2 \times 10^9 \text{ s}^{-1}$; $k_{\text{CR}} = 6.8 \times 10^6 \text{ s}^{-1}$).^{17,18} Although the large donor-acceptor distances are comparable in (i) to (iv), different electronic couplings were observed, as indicated by varying charge separation and charge recombination features (*i.e.*, rates, efficiencies, quantum yields, *etc.*). The π -stacked ZnP- C_{60} conjugate may be considered as a point of reference. Here, van der Waals contacts promote significantly faster picosecond dynamics.¹⁹

In the aforementioned DBA conjugates the efficiency of the charge transfer process decreases exponentially with increasing bridge length. Long-range electron transfer processes, which in these conjugates occur *via* superexchange, are typically limited to distances of approximately 20 Å. Above these distances the rate-determining electronic coupling is largely diminished and, consequently, insufficient to compete with the intrinsic excited state deactivation of the electron donor.

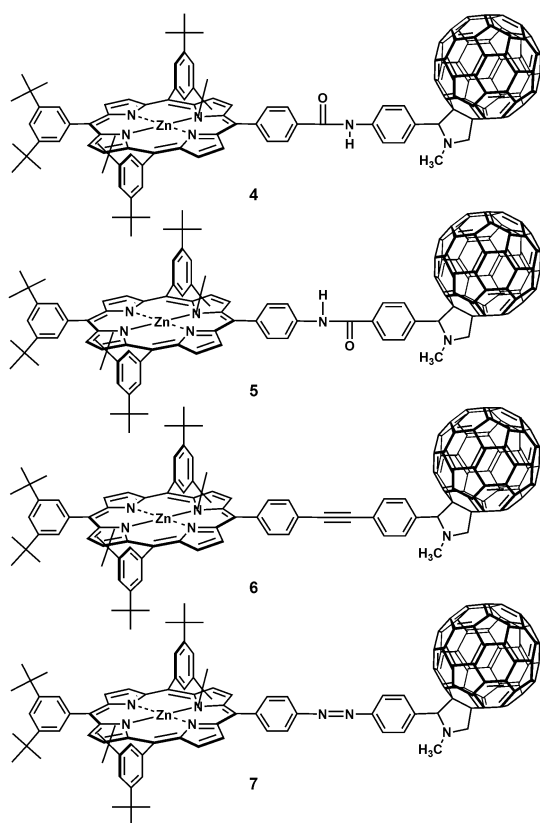


Fig. 2 Chemical structures of ZnP-C₆₀ conjugates 4–7.

The transport of charges over distances beyond 20 Å requires, however, alternative concepts. This task becomes particularly relevant for the generation of ultralong radical ion pair lifetimes. One viable option to achieve charge separation over large distances utilizes a relay of several short-range

electron-transfer events along well-designed redox gradients rather than transferring the electrons in one single, concerted long-range step.

Such a “relay concept” was successfully realized by combining several different redox-active building blocks—ferrocene (Fc) to ZnP to free-base tetraphenylporphyrin (H₂P) and to C₆₀—to form Fc–ZnP–H₂P–C₆₀ and Fc–ZnP–ZnP–C₆₀ conjugates.^{20,21} Fig. 3 summarizes some leading examples, where the first electron donor units (*i.e.*, Fc) and the ultimate electron acceptors (*i.e.*, C₆₀) are separated by nearly 50 Å. In these novel molecular architectures we demonstrated very slow intramolecular charge recombination processes—observable only by ESR measurements in frozen matrices under light irradiation. When comparing Fc–ZnP–H₂P–C₆₀ (0.38 s) or Fc–ZnP–ZnP–C₆₀ (1.6 s) conjugates with analogous H₂P–C₆₀ or ZnP–C₆₀ conjugates, the difference in radical ion pair lifetimes amounts to six orders of magnitude, *i.e.* seconds *vs.* microseconds.

Primarily, low electronic coupling elements guarantee such outstanding lifetimes. The couplings, V , are as small as $(5.6 \pm 0.5) \times 10^{-5} \text{ cm}^{-1}$ relative to $7.9 \pm 1.7 \text{ cm}^{-1}$ seen for the ZnP–C₆₀ conjugates, where the electron–donor–acceptor separations are $\sim 12 \text{ \AA}$. These findings correlate well with negligible orbital overlap—an argument that finds further support when calculating the attenuation factor (β). A plot of the radical ion pair lifetimes of Fc–ZnP–H₂P–C₆₀ ($\sim 50 \text{ \AA}$), ZnP–H₂P–C₆₀ ($\sim 30 \text{ \AA}$) and H₂P–C₆₀ ($\sim 12 \text{ \AA}$) *vs.* electron–donor–acceptor separation is well fitted with a straight line and yields a β value of 0.60 \AA^{-1} .

Importantly, such a β value is located within the boundaries of nonadiabatic electron transfer reactions for saturated hydrocarbon bridges ($0.8\text{--}1.0 \text{ \AA}^{-1}$) and unsaturated phenylene bridges (0.4 \AA^{-1}).^{22,23}

In light of long-range electron-transfer processes, *para*-conjugated molecular wires emerged as particularly striking

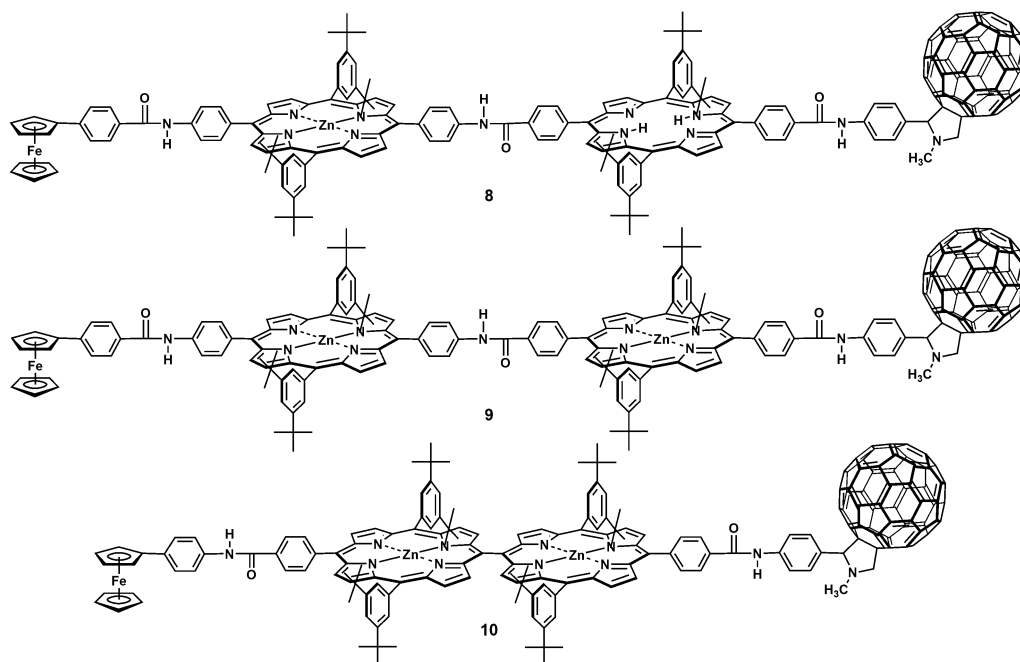


Fig. 3 Structures of Fc–ZnP–H₂P–C₆₀, and Fc–ZnP–ZnP–C₆₀ conjugates.

candidates, since they seem not to actively participate in the electron-transfer events (*i.e.*, charge separation, charge recombination, charge hopping, *etc.*). In other words, *para*-conjugated molecular wires play a real mediating role in the transport of charges due to their well-isolated high-lying LUMO and/or low-lying HOMO orbitals.

p-Phenylenevinylene, alkyne and *p*-phenyleneethynylene oligomers turned out to be versatile model bridges with chemically tailored properties. Accordingly, we and others have tested a series of novel electron-donor–acceptor conjugates that incorporate ZnP as electron donors and C₆₀ as electron acceptors, linked by *p*-phenylenevinylene (ZnP–*p*-phenylenevinylene–C₆₀),²⁴ alkyne (ZnP–alkyne–C₆₀),²⁵ and *p*-phenylenebutadiynylene oligomers (ZnP–*p*-phenylenebutadiynylene–C₆₀) of variable length²⁶ (see Fig. 4). Notable in this context is the connection of *p*-phenylenevinylenes, alkynes and *p*-phenylenebutadiynylenes to the ZnP's phenyl group. The following aspects were considered at the forefront of our investigations: (i) systematic variation of the length of the π -conjugated system; (ii) determination and evaluation of the structural (*i.e.*, donor–acceptor separation) and electronic (*i.e.*, energy levels) effects on the charge-transfer rates; (iii) testing the molecular-wire behavior in *p*-phenylenevinylene, alkyne or *p*-phenylenebutadiynylene based DBA ensembles in terms of attenuation factors.

For ZnP–*p*-phenylenevinylene–C₆₀ (**11a,b**), a detailed physico-chemical investigation—probing mainly long-range charge separation (in THF: rate = $3.9 \pm 0.6 \times 10^9 \text{ s}^{-1}$) and charge recombination events (in THF: rate = $1.05 \pm 0.15 \times 10^6 \text{ s}^{-1}$) including their kinetics—revealed attenuation factors of $0.03 \pm 0.005 \text{ \AA}^{-1}$. Even in comparison to *p*-phenylene (*i.e.*, $0.32\text{--}0.66 \text{ \AA}^{-1}$), polyene (*i.e.*, $0.04\text{--}0.2 \text{ \AA}^{-1}$) and polyynes (*i.e.*, $0.04\text{--}0.17 \text{ \AA}^{-1}$), such β values are extraordinary small.^{27–30} Vital for the wire-like behavior is that the energies of the HOMO of C₆₀ match those of the long *p*-phenylenevinylene bridges. This facilitates charge injection into the wire. Equally important is the strong electronic coupling, realized through the *para*-conjugation in *p*-phenylenevinylenes. This leads to donor/acceptor coupling constants of $\sim 2.0 \text{ cm}^{-1}$ —even at electron donor–acceptor separations

of 40 \AA —and assists electron transfer reactions that reveal shallow distance dependences. Remarkable is the fact that these features are realized despite the rotational freedom of the donor–bridge and bridge–acceptor contacts. To analyze the charge recombination mechanism the radical pair lifetimes were probed between 268 and 365 K. The Arrhenius plots can be separated into two distinct sections: the low-temperature regime (*i.e.*, $<300 \text{ K}$) and the high-temperature regime (*i.e.*, $>300 \text{ K}$). The weak temperature dependence in the 268 to 320 K range suggests that a stepwise charge recombination may be ruled out, leaving electron tunneling *via* superexchange as the operative mode. This picture is in sound agreement with the thermodynamic barrier, necessary to overcome in forming ZnP–*p*-phenylenevinylene^{•+}–C₆₀^{•-}. At higher temperatures (*i.e.*, $>300 \text{ K}$) the situation changes and the charge recombination is accelerated. The observed strong temperature dependence suggests a thermally activated charge recombination. The activation barriers (E_a), derived from the slopes (*i.e.*, between 0.2 eV), confirm the HOMO (C₆₀) – HOMO (wire) energy gap.

Somewhat larger are, however, the attenuation factors (*i.e.*, $0.06 \pm 0.005 \text{ \AA}^{-1}$) determined for polyalkyne bridges in ZnP–alkyne–C₆₀ (**12a,c**) with charge separation and charge recombination rates in the order of $7.5 \pm 2.4 \times 10^9 \text{ s}^{-1}$ and $1.6 \pm 0.2 \times 10^6 \text{ s}^{-1}$, respectively. Nevertheless, these findings prove that even triple bonds are effective mediators of long-range electronic interactions up to nearly—but not limited to— 24 \AA . An interesting aspect of this work was that the direct linkage between the polyalkyne wires and C₆₀ provides much better bridge–acceptor contacts.

Electron transfer features have also been successfully demonstrated for a ZnP–*p*-phenylenebutadiynylene–C₆₀ series (**13a,c**) with effective center-to-center donor–acceptor distances ranging from 20 to 40 \AA . In comparison with the ZnP–*p*-phenylenevinylene–C₆₀ and ZnP–alkyne–C₆₀ conjugates, the significantly higher attenuation factor of 0.25 \AA^{-1} prompts to a less effective superexchange mechanism due to the alternating bond lengths—double *vs.* triple bonds.

The aforementioned results corroborate effective charge mediating properties of *p*-phenylenevinylene, alkyne and

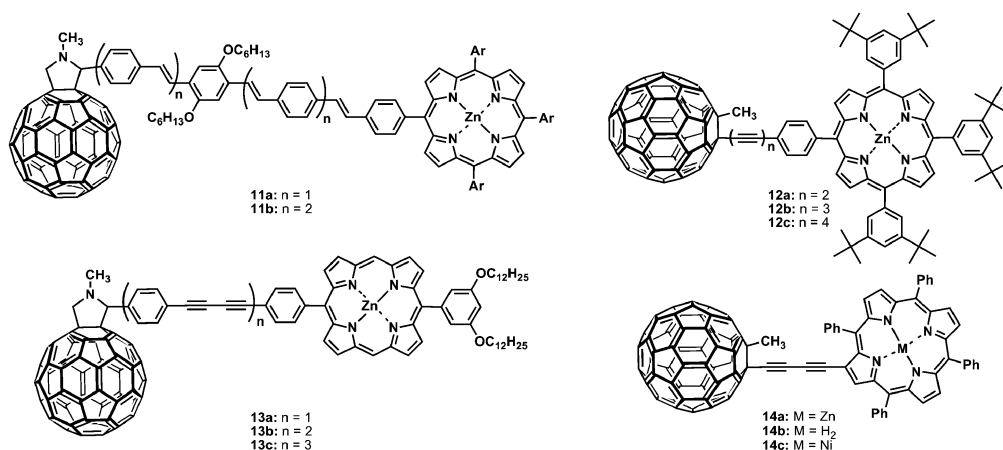


Fig. 4 Chemical structure of some ZnP–*p*-phenylenevinylene–C₆₀, ZnP–alkyne–C₆₀ and ZnP–*p*-phenylenebutadiynylene–C₆₀ electron donor–acceptor conjugates.

p-phenylenebutadiynylene oligomers. Nonetheless, some subtle differences emerge. To shed light onto this aspect, we have varied the substitution pattern of ZnP.³¹ In particular, placing the polyalkyne at the β -position (**14a,c**) notably affects the electronic coupling. Examining the molecular orbitals suggests a strong propensity for intramolecular electron transfer from ZnP to C₆₀ following photoexcitation. To this end, the β -substituted polyalkyne gives rise to a much faster charge recombination (in THF: $1.0 \pm 0.5 \times 10^{10} \text{ s}^{-1}$) process due, at least in part, to more favorable orbital interactions between ZnP and C₆₀. However, no attenuation factor was determined.

Quite a contrasting picture was found in β -substituted ZnP-*p*-phenyleneethynylene-C₆₀ (**15a,b**) (Fig. 5). Specifically, charge separation occurs in polar media affording a charge separated state but the lifetimes tend to increase with increasing distance between the two photoactive units. In regard to donor-acceptor separations of up to 23 Å, it is safe to assume a through-bond mechanism, where the bridge plays a crucial role. The studied conjugates indicate a linear dependence of the electron transfer rate constant on the donor-acceptor distance and yield an attenuation factor of 0.11 \AA^{-1} . Again, implementing triple bonds between the phenyl groups impacts the extended π -conjugation and, in turn, the charge transfer properties.

Furthermore, solely one analogous ZnP(H₂P)-*p*-phenylenevinylene-C₆₀ (**16a,b**)-2-mer has been synthesized and investigated.³² Photophysical studies revealed that efficient electron transfer processes upon photoexcitation afford the corresponding radical ion pairs of ZnP(H₂P)-*p*-phenylenevinylene-C₆₀. The results confirm that β -substitution on the

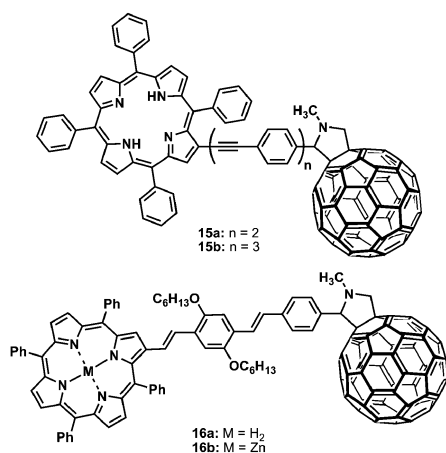


Fig. 5 β -Substituted ZnP-*p*-phenyleneethynylene-C₆₀ and ZnP(H₂P)-*p*-phenylenevinylene-C₆₀.

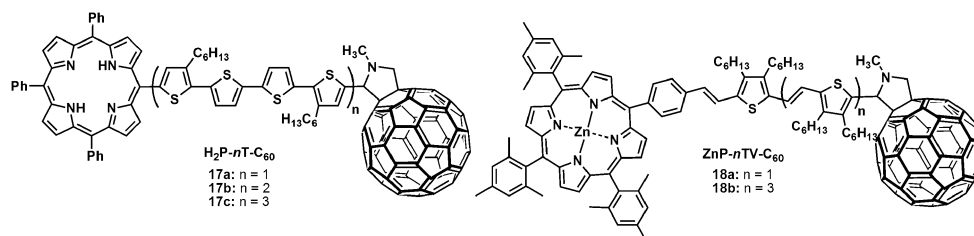


Fig. 6 H₂P-oligothiophene-C₆₀ and ZnP-oligothiophenevinylene-C₆₀ donor-acceptor conjugates.

porphyrin moiety favors the electronic coupling and the electronic communication between the donor and acceptor units. Work is currently in progress to prepare related conjugates with varying length of the *p*-phenylenevinylene bridge to determine the attenuation factor in these β -substituted conjugates.

We encounter a quite different situation in H₂P-thiophene-C₆₀ conjugates (**17a,c**) (Fig. 6). Here, different thiophene oligomers are directly linked to the *meso* position of H₂P affording electron donor-acceptor distances of up to 55.7 Å.^{33,34} Furthermore, the electron donating properties of polythiophene alter the photoreactivity in H₂P-thiophene-C₆₀, *i.e.*, the bridges actively participate in the electron transfer processes. Not surprisingly, the attenuation factors varied with solvent polarity: 0.11 \AA^{-1} in *o*-dichlorobenzene and 0.03 \AA^{-1} in benzonitrile.

Common to the aforementioned conjugates is that in temperature dependent measurements the charge recombination kinetics imply an efficient decoupling of the donor-bridge and bridge-acceptor contacts, which leads to a significant slow-down of the electron transfer rates. Reversible interruption of the π -conjugation through temperature-induced rotations along the wire axis is believed to be responsible for this effect.

Oligothiophenevinylens (*n*TV) of different length have also been reported as molecular wires which connect ZnP to C₆₀.³⁵ For **18a,b** (Fig. 6) with $n = 1$, energy transfer prevails over charge separation in nonpolar solvents. In polar PhCN, on the other hand, charge-separation occurs predominantly due to the stabilization of the radical ion pair state by polar solvent molecules. In case of longer *n*TV bridges ($n = 3$) and nonpolar solvents, charge separation surpasses energy transfer. The decrease of k_{CS} with increasing length of the wire gives rise to a relatively small damping factor for the charge-separation process.

Enthrallingly challenging is the incorporation of oligomeric bridges, in which the π -conjugation is irreversibly broken off by, for instance, the chemical nature of the bridge structure.³⁶ Chiral binaphthyl derivatives meet such criteria and are also used as electroactive species (Fig. 7). In contrast to conjugated *p*-phenylenevinylene oligomers, the π -conjugation between the two naphthyl units is effectively disrupted *via* atropisomerism. Consequently, distances and electronic interactions between donor and C₆₀ are drastically changed.

In fact, we have found that topological effects of the geometrically well-defined chiral binaphthyl spacer play a leading role in the electronic interactions in these donor-acceptor ensembles. Thus, in ZnP-binaphthyl-C₆₀ (**19**),

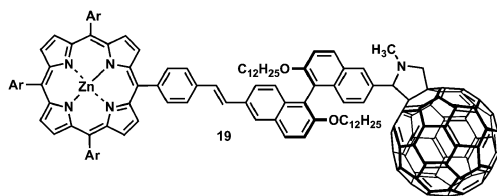


Fig. 7 Chemical structure of ZnP–binaphthyl–C₆₀.

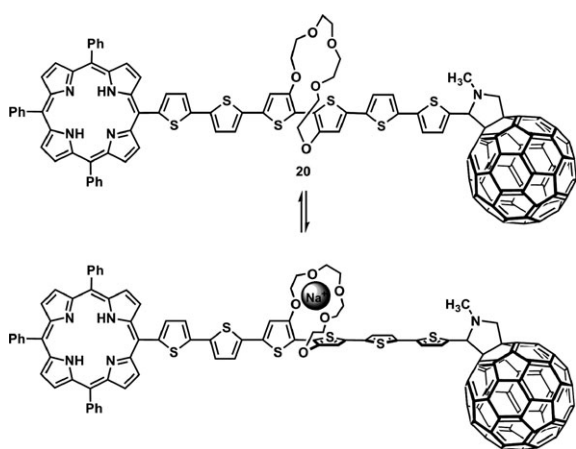
associative π – π interactions augmented by electron transfer interactions favor a conformer in which the ZnP is close to C₆₀. Such a conformation gives rise to appreciable through-space electronic communication with charge recombination dynamics in the order of $\sim 10^6$ s⁻¹.

Reversible interruption of π -conjugation, on the other hand, may be used to control the electron transfer properties of molecules (gate function). In this context, Ito *et al.*³⁷ reported the synthesis of a H₂P–sexithiophene–C₆₀ (**20**) where the two central thiophene units of the sexithiophene spacer are bridged by a crown-ether-like polyether chain. In **20**, the photoinduced electron transfer is entirely governed by complexation/decomplexation of a sodium cation in the crown ether ring. As a consequence it operates as a complexation-gated molecular wire (Scheme 1).

In conclusion, the investigations focusing around ZnP–C₆₀ electron donor–acceptor ensembles were ground breaking by revealing attenuations factors that varied with the nature of the oligomers. A big plus of ZnP–C₆₀ conjugates is their simplicity in photoactivity, namely, selective ZnP photoexcitation is followed by intramolecular charge separation and charge recombination. Nevertheless, structural aspects such as the ZnP substitution pattern (*i.e.*, *meso*-substitution or β -substitution) seem to highly impact the underlying charge transfer processes.

2.2 C₆₀–wire–*ex*TTF systems

Bearing the aforementioned conjugates in mind, C₆₀–*ex*TTF conjugates offer the great advantage of linking the oligomeric bridge to *ex*TTF without compromising the π -conjugation (Fig. 8). Particularly, extended π -conjugation is ensured between the anthracenoid part of the *ex*TTF-donor,



Scheme 1 Sexithiophene as a complexation-gated molecular wire in H₂P–sexithiophene–C₆₀ systems.

the oligomeric bridge (*i.e.*, *p*-phenylenevinylenes, *p*-phenyleneethynyls or oligofluorenes), and the pyrrolidine ring of the C₆₀ derivative.

C₆₀–*p*-phenylenevinylene–*ex*TTF systems (**21**)^{38,39} exhibit charge separation processes over distances of up to 50 Å. The outcome is the respective radical ion pair. Interestingly, the radical ion pair lifetimes are in the range of 465 ns to 557 ns, which indicates shallow dependence of the electron-transfer rate on the length of the oligomeric bridge. In the corresponding 7-mer the radical ion pair lifetimes turned out to be 10-times longer, which has been attributed to the loss of planarity of the bridge moiety. The dihedral angles between the two terminal benzenes were calculated to 38°. Plotting the electron transfer kinetics as a function of donor–acceptor distance led to linear dependences in THF and benzonitrile. An extraordinarily small attenuation factor of only 0.01 ± 0.005 Å⁻¹ was determined from the slope of these plots. Pivotal for the observed wire-like behavior is the coupling constant (*V*) with values of ~ 5.5 cm⁻¹, which is peculiarly strong considering that the donor and acceptor sites are separated by a distance of 40 Å.

Similarly, in C₆₀–*p*-phenyleneethynylene–*ex*TTF systems (**22**)^{40,41} transient absorption spectroscopy confirmed the presence of spectral signatures of the one-electron oxidized *ex*TTF^{•+} radical cation and the one-electron reduced C₆₀^{•-} radical anion. These findings hold, however, only for the 1-mer and 2-mer, while in the 3-mer no radical ion pair formation was evidenced.

Relating the charge separation and charge recombination dynamics in THF to the donor–acceptor distance provided an attenuation factor for the *p*-phenyleneethynylene bridges of 0.2 ± 0.05 Å⁻¹. Extrapolating the linear relationship to the center-to-center distance of the 3-mer results in a charge separation rate that would be notably slower than the intrinsic deactivation of the C₆₀ singlet excited state. This, in turn, helps to rationalize the lack of electron transfer in the 3-mer. To shed light onto the higher values of the attenuation factor, we conducted calculations that revealed a few trends. First, the molecular geometry of the C₆₀–*p*-phenyleneethynylene–*ex*TTF conjugates does not exhibit a significant deviation from planarity (less than $\pm 12^\circ$), thus allowing the electronic coupling between the donor and acceptor units. Secondly, scrutinizing the electronic structure unveils that the HOMO in C₆₀–*p*-phenylenevinylene–*ex*TTF (**21**) reaches into the *p*-phenylenevinylene bridge, whereas the HOMO in the C₆₀–*p*-phenyleneethynylene–*ex*TTF (**22**) is completely localized on the *ex*TTF. Thus, charge injection into the bridge is much easier in **21** than in **22**. Thirdly, local electron affinity mappings evidence a homogenous distribution of electron affinity throughout the whole bridge in C₆₀–*p*-phenylenevinylene–*ex*TTF, whereas in the *p*-phenyleneethynylene systems local maxima were found on the phenyl rings and minima on the triple bonds. This points to the polarizing character of the triple bonds and their shorter bond length. In comparison to the pure double bond character of the *p*-phenylenevinylene bridges, the bond length alternation caused by the presence of triple bonds in C₆₀–*p*-phenyleneethynylene–*ex*TTF (**22**) disrupts the extended π -conjugation and strongly influences the charge separation.

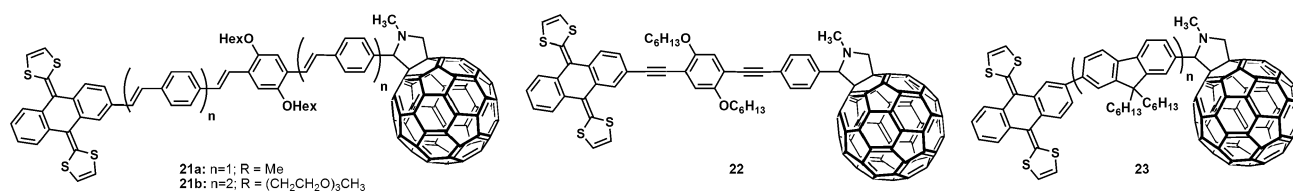


Fig. 8 Examples of $\text{exTTF-oligomer-C}_{60}$.

Finally, from the linear dependence of the rate constants (*i.e.*, 10^9 s^{-1} for charge separation and 10^5 s^{-1} for charge recombination) on distance in C_{60} -oligofluorene- exTTF (**23**)⁴² (Fig. 8) an attenuation factor of 0.09 \AA^{-1} emerged. In other words, the ability to conduct charges in oligofluorenes lies between that of *p*-phenylenevinylens and that of *p*-phenylenethynylens. DFT calculations predict fairly good electronic communication between exTTF and C_{60} . The HOMO and LUMO energies of exTTF and the oligofluorene building blocks, respectively, evidently match each other, providing a good orbital overlap between the donor and the bridge. Electron affinity calculations also confirm the electron transfer pathway from the donor over the bridge to the fullerene acceptor in C_{60} -oligofluorene- exTTF . A homogenous distribution of electron density throughout the whole molecule and a channel of high local electron affinity through the bifluorene bridge that maximizes at C_{60} prove the charge-transfer features of these systems.

2.3 C_{60} -wire-Fc systems

An interesting alternative involves testing the charge-transfer efficiencies of polyporphyrin bridges that are linked *via* butadiynes (Fig. 9).⁴³ In that sense a series of Fc-porphyrin- C_{60} conjugates (**24a,c**) (*i.e.*, 1-mer, 2-mer and 4-mer) were investigated. Photoexcitation of the polyporphyrin results in the formation of spatially separated radical ion pair states. The formation occurs *via* a sequence of electron transfer steps. Charge separation and charge recombination rates were elucidated utilizing transient absorption and fluorescence spectroscopic tools. The charge recombination rates are remarkably fast (*i.e.*, $15\text{--}1.3 \times 10^8 \text{ s}^{-1}$)—a consequence that stems from bridge-mediated electronic couplings. Plotting the charge recombination rates *vs.* donor-acceptor distances fails in providing a straightforward relationship. Nevertheless, it is plausible to separate the data points into two groups. The slope of a line that connects the first two data points (*i.e.*, shorter bridges) corresponds to an attenuation factor of 0.18 \AA^{-1} . This value is in the lower end of those typically found for conjugated bridge structures and indicates weak distance dependence. On the other hand, connecting the

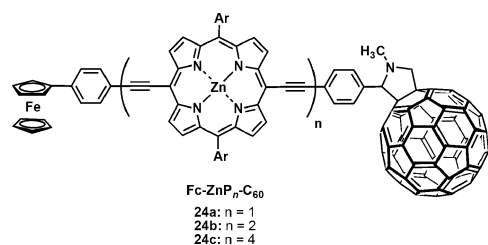


Fig. 9 Fc-ZnP- C_{60} electron donor-acceptor systems.

second and third data points (*i.e.*, longer bridges) results in a line with practically no distance dependence ($\beta = 0.003 \text{ \AA}^{-1}$). The long-range charge recombination process seems to occur *via* electron tunneling rather than *via* hopping or triplet recombination. Obviously, the distance dependence of the electron transfer processes in these conjugates should not be considered as a single parameter for the charge-transfer efficiency and the exact mechanism still remains to be elucidated. However, the observation that the 4-mer mediates long-range charge transfer over a distance of 65 \AA is essential for the application of such structures as molecular wires.

The use of π -conjugated oligomers to link fullerenes to electron donating ferrocenes leads to further examples of donor-acceptor conjugates. Hereby, the radical cations are delocalized over the donor and the linker. This, in turn, affects the charge separation and charge recombination dynamics in a favorable manner. However, no distance dependence has been tested in such systems.^{44,45}

Extending the scope of earlier studies on **25** (Fc- $n\text{T-C}_{60}$) paved the way for recent studies on **26** (Fc-tm- $n\text{T-C}_{60}$) (Fig. 10).⁴⁶ In the latter, a trimethylene (tm) fragment has been inserted between the ferrocene and the oligothiophene moieties, which perturbs the conjugation between the two chromophores. Time-resolved fluorescence and transient absorption spectroscopy of Fc- $n\text{T-C}_{60}$ disclosed that the excited state deactivation in non-polar toluene occurs exclusively *via* energy transfer. This process evolves from the ^1nT formation and results in the generation of $^1*\text{C}_{60}$. In polar benzonitrile, on the other hand, charge separation is thermodynamically favored. A radical cation is generated instantaneously. Interestingly, the positive charge is delocalized over the Fc and $n\text{T}$ moieties ((Fc- $n\text{T}$) $^{+\bullet}$ - $\text{C}_{60}^{\bullet-}$). Upon systematic variation of the spacer length, $n\text{T}$, from 4T to 12T, the lifetimes of (Fc- $n\text{T}$) $^{+\bullet}$ - $\text{C}_{60}^{\bullet-}$ increased accordingly from 0.1 to 50 ns. In general, the varying oxidation potentials of the $n\text{T}$

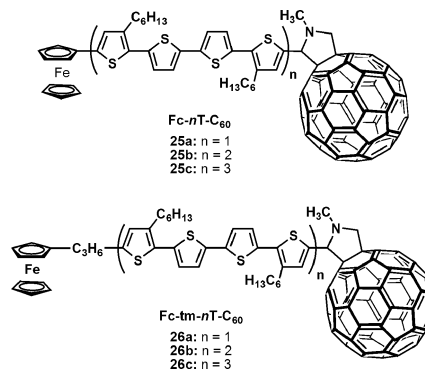


Fig. 10 Chemical structures of Fc- $n\text{T-C}_{60}$ (**25**) and Fc-tm- $n\text{T-C}_{60}$ conjugates and (**26**).

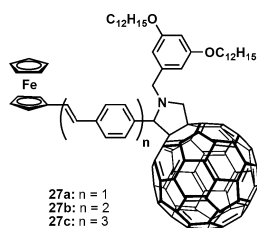


Fig. 11 Structure of Fc-*p*-phenylenevinylene- C_{60} (27).

moieties seem to control the electron transfer processes. Considering the *tm*-extended conjugates, Fc-*tm-nT*- C_{60} , a change in reactivity was observed in polar solvents. Charge separation—to yield initially Fc-*tm-nT* $^{\bullet+}$ - $C_{60}^{\bullet-}$ —involved an energy transfer scenario, in which Fc-*tm-¹nT*- C_{60} deactivates *via* Fc-*tm-nT-¹*C₆₀*. Nevertheless, the positive charge shifted from *nT* $^{\bullet+}$ to Fc producing Fc $^{\bullet+}$ -*tm-nT*- $C_{60}^{\bullet-}$. The latter lasted up to 330 ns when replacing 4T with 12T. The longer lifetimes of Fc $^{\bullet+}$ -*tm-nT*- $C_{60}^{\bullet-}$ compared to those of (Fc-*nT*) $^{\bullet+}$ - $C_{60}^{\bullet-}$ are rationalized by the presence of the trimethylene chain, which, in turn, disrupts the conjugation between the Fc and the *nT* moieties (Fig. 10). β was evaluated for Fc-*tm-nT*- C_{60} utilizing the corresponding donor acceptor distances obtained from the optimized structures. In benzonitrile, for example, a value of 0.10 \AA^{-1} was obtained. Notably, the attenuation factor β is significantly higher than for the corresponding H_2P -*nT*- C_{60} conjugates, with a value of 0.03 \AA^{-1} . In the latter, H_2P and *nT* are directly connected, pointing, once again, to the critical role of the linkage between the donor and the bridge.

C_{60} -bridge-Fc arrays (27a-c) in which a fulleropyrrolidine and a ferrocene units are connected *via* an oligo-*p*-phenylenevinylene bridge, have also been studied (Fig. 11). Photophysical studies show a complete quenching of the fluorescence of organic conjugated moieties in 27a-c *via* energy transfer to the Fc unit. In the more complex C_{60}/Fc arrays, the quenching of the C_{60} moieties is ultrafast in CH_2Cl_2 solution and most likely attributable to electron transfer *via* the *p*-phenylenevinylene wire. In toluene, the dynamic process of singlet and triplet fullerene quenching can be traced *via* time-resolved fluorescence and transient absorption spectroscopy and the values of the rate constants are smaller with increasing donor-acceptor distance. However, a definitive assignment of the intercomponent quenching mechanism between the fullerene and the ferrocene moiety (energy or electron transfer) was not obtained due, probably, to the competition of the C_{60} -Fc singlet-triplet and triplet-triplet energy transfer with the charge separation process.⁴⁷

3. Fullerenes as molecular wires

Turning to recent developments of ideal molecular wires, several milestones toward molecular-scale electronic devices have already been passed regarding the transduction of electrons through single molecules.⁴⁸⁻⁵⁰ Implicit are experimental conditions that guarantee molecular conduction through a single molecule rather than through an ensemble of molecules. Moreover, to eliminate cooperativity in transport and to avoid equalizing the conduction through molecules in different conformations are important incentives.

The feasibility of utilizing single molecules as active elements in electronic devices offers myriad opportunities. To demonstrate these principles, a series of recent experiments have documented electron transport through single molecules. One of the main challenges in this field is the development of techniques that assist in reproducibly “wiring up” single molecules. Up to now, scanning probe microscopy techniques—STM or AFM—have been widely employed in conductance measurements in single molecule set-ups.^{51,52} As a viable alternative mechanical break junctions have emerged in a series of groundbreaking experiments.^{53,54} More recently, other approaches were brought forward. One of these includes the fabrication of electrodes that are spaced by nanometer scale gaps. These gaps are sufficiently small to “wire up” molecules in a planar geometry. With the help of these techniques, Diederich, Calame and co-workers⁵⁵ have measured electronic transport through thiolated C_{60} derivatives. To this end, a two-probe configuration was provided by the tips of a break junction (Fig. 12). Single functional groups at the termini of the electrodes serve as anchors and affirm the trapping of single molecules between the gold contacts. Of interest is the fact that one may control the coupling of C_{60} to the gold electrode by mechanically adjusting the inter-electrode spacing d in a liquid environment. Obviously, the environment combined with a certain geometry, exerts a strong impact on the tunneling rates between the gold electrode and C_{60} . These pioneering results—together with the capability of modifying the linker groups—afford valuable insight into the electronic coupling between molecules and electrodes in molecular devices.

On the other hand, Nishino, Ito and Umezawa⁵⁶ have constructed molecular tips for STM which are based on C_{60} . Those tips were prepared by chemically modifying a corresponding metal tip. As a result, electron tunneling events involve the outermost single adsorbate probes and the sample molecule. Importantly, a clear trend was found between the tunneling current and the tip-sample interactions. Metal coordination or hydrogen-bonding interactions, for example, provide the required overlap between the electronic wave functions of the porphyrin and C_{60} and, thus, gate/facilitate the tunneling current. In this context, Ito and co-workers have been able to detect electron tunneling within single ZnP/ C_{60} , CoP/ C_{60} and H_2P/C_{60} associates (Fig. 13). For instance, charge-transfer interactions between CoP- and C_{60} -modified tips involve the highest occupied molecular orbital (HOMO) of CoP and lowest unoccupied molecular orbital (LUMO) of the C_{60} tip. The former and the latter are high and low in energy, respectively. Such an energy relationship is considered

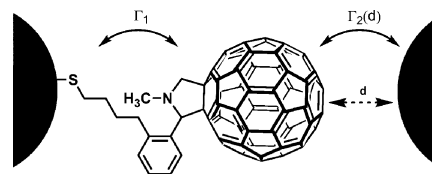


Fig. 12 Schematic representation of a break junction with a thiolated C_{60} molecule anchored to the left electrode. The distance d between the molecule and the right electrode can be adjusted by opening and closing the junction.

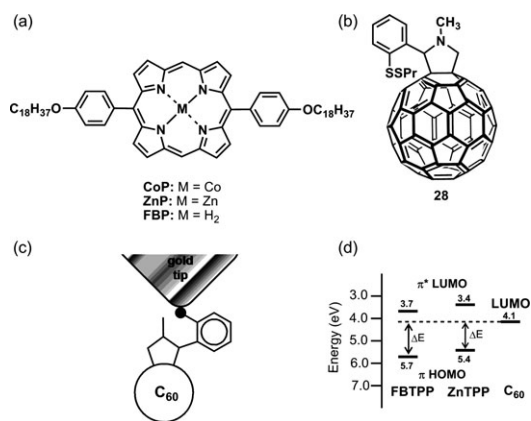


Fig. 13 Chemical structures of the porphyrins (a) and fullerene derivative (b) used as precursors of the molecular tip. Schematic representation of the molecular tip (c). Energy diagram of free-base and zinc(II) tetraphenylporphyrin (FBTPP and ZnTPP, respectively) and fullerene (C_{60}) (d).

to be the basis for directive electron flow when applying a finite voltage. Particularly striking in these experiments was that electron tunneling indeed occurred exclusively from CoP to C_{60} —but not in the opposite direction. It has been further demonstrated that such localized tunneling provides a method to visualize the frontier orbitals of CoP and evaluate their energies. Moreover, rectified tunneling was observed in the polarity dependence of the STM images and the I - V curves. This, in turn, indicates that the MP/ C_{60} pair constitutes a molecular rectifier.

A field-effect transistor-like behaviour has recently been reported in fullerene-substituted mixed-valence bis(ferrocenylethynyl)ethene derivatives in which the electronic interactions between the electroactive species are modulated by through-space intramolecular interactions of the C_{60} with the conjugated system.⁵⁷

Conclusions

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. In this light, the selected examples described in this review illustrate the exponentially increasing interest—experimental, theoretical, and technological aspects—and potential of molecular wires as multifunctional building blocks in well-ordered multicomponent conjugates/hybrids. If a molecular computer is ever to be built, then it will need molecular wires, and these will have to be connected to its various components. Molecular wires possess exciting mechanical, optical and electrical properties that would seem to make them ideal nanoscale materials. But despite this great promise, chemists/materials scientists/physicists have encountered great problems in actually working with molecular wires. Thus, the systematic exploration of these systems should surely be regarded as breakthroughs in light of implementing molecular wires into new optoelectronic devices—including molecular electronics, printable electronics, *etc.*

Noteworthy is the recent introduction of elegant and versatile protocols concerning the chemical functionalization of π -conjugated oligomers of precise length and constitution. In fact, some of the aforementioned limitations can be easily overcome through the controlled covalent functionalization of the molecular wire's termini. This includes, for example, attaching covalently linked molecular 'handles' that serve ultimately as sources and drains for charge carriers. Previous work has eluded how the connection between molecular building blocks and electrodes greatly affects the current-voltage characteristics. Again, we believe that the control over handling the linkage emerged as a key asset.

Besides the outreach into the field of molecular electronics, the design and development of light harvesting, photoconversion, and—as a long term aim—catalytic modules should not be overseen. They should be capable of self-ordering and self-assembling into integrated functional units, which will render it possible to realize efficient artificial photosynthetic systems.

In summary, it is fair to emphasize that the 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. If the more technological problems can be solved, there is an almost unlimited field of application to be foreseen and eventually molecular wires may become important building blocks in emerging technologies. In a more visionary view these nanoscale molecular wires may help minimize computer circuit dimensions and enhance performance.

Nevertheless, we wish to close with a recent statement by Nitzan and Ratner⁴⁸ "...Despite several experimental and theoretical advances, including the understanding of simple systems, there is still limited correspondence between experimental and theoretical studies of these systems..."

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