Charge Transport at the Metal-Organic Interface

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Abstract

This review focuses on the impacts of metal-organic interfacial bonding interactions on the charge-transport dynamics involved in molecular junctions as well as organically capped nanoparticles. Whereas mercapto derivatives have been used extensively as the ligands of choice to functionalize metal and nanoparticle surfaces with the formation of metal-thiolate interfacial bonds, recent studies show that metal-carbon covalent linkages may be fabricated by the deliberate design and selection of functional moieties. With enhanced electronic interactions between metals and organic ligands, the interfacial contact resistance diminishes drastically, leading to the emergence of unprecedented optical and electronic properties of the junctions and nanoparticles. These mechanistic insights are of fundamental significance in the development of molecule- and nanoparticle-based electronic devices, in particular, in light of the diverse metal-nonmetal bonding interactions that have been extensively observed in organometallic chemistry.

Keywords
metal-ligand contacts, molecular junctions, organically capped nanoparticles, intraparticle charge delocalization
1. INTRODUCTION

Electronic circuits based on simple molecules or nanostructures represent an effective and attractive solution to the grand challenge of continuing diminishment of feature size with ever-enhanced performance, a concept pioneered by Aviram & Ratner (1). Within such a framework, simple organic molecules or nanostructures (e.g., nanoparticles, nanotubes, nanowires) serve as the active components to achieve the diverse functionalities of circuit elements in manipulating electrical outputs, analogous to silicon-based semiconductor materials, by taking advantage of the ready manipulation of their structures and properties through molecular design and nanoscale engineering. In these devices, the circuit elements are generally in contact with a metal lead, with the interfacial contact possibly playing a critical role in determining device performance. For instance, in molecular electronics represented by a nanojunction bridged by a thin film of organic molecules, it is well known that the junction conductance can be manipulated not only by the chemical backbones of the organic molecules but also by the metal-molecule bonding contacts and molecule-molecule interactions (2–6). In these, depending on the terminal structures and hence the metal-molecule hybridization, the interfacial contact may exhibit ohmic behaviors or may behave as a Schottky barrier for charge transfer (7–10).

Such a variation of the metal-organic bonding interactions and hence interfacial contact resistance is also anticipated to impact the charge-transfer properties of organically capped transition-metal nanoparticles (11–16). Whereas a number of studies have been carried out both at the single-particle level and with particle ensembles (17–26), most are focused on mercapto derivatives as the ligands of choice for nanoparticle surface functionalization because of the strong affinity of thiol groups to metal surfaces. Recently a series of studies demonstrated that other metal-organic bonding linkages can be readily produced. This not only affects the growth dynamics of the nanoparticles (27), but more interestingly also controls the spilling of core electrons into the organic matrix and hence the energetic barrier for interparticle and intraparticle charge transfer (vide infra). One can see that understanding such nanoscale electron transfer is fundamentally significant in the use of nanoparticles as structural units in the fabrication of new functional nanodevices.

Whereas the structural configurations may differ drastically between the molecular junctions and the nanoparticles, both exhibit a clearly defined metal-organic interface, and there is a significant overlap of the fundamental mechanisms that govern the interfacial electron transfer. Thus in this review article we summarize some of the latest progress in the investigation of metal-ligand interfacial contacts on the charge-transfer characteristics in two systems (nanojunctions and nanoparticles) and then highlight some emerging challenges and possible future directions.

2. MOLECULAR JUNCTIONS

The simplest form of a nanojunction consists of two metal electrode leads that are positioned with a nanoscale gap and bridged by a single organic molecule or a thin film of organic materials (6). The junction is typically decomposed into three individual barriers through the molecular body and metal-molecule contacts on both sides of the molecules, and the metal-molecule contacts are generally separated from the molecular body (28), when the applied bias is much lower than the HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital) gap of the molecule and the junction barrier height, and nonresonant tunneling is the main mechanism of charge transport.

There are several leading approaches to the preparation of nanojunction electrodes. The first involves so-called break junctions, in which a nanogap is produced by breaking a metal wire through mechanical pulling, chemical etching, or electromigration (29, 30–35). The second entails
controlled etching of a metal thin film by, for instance, electron-beam lithography (36). Once a gap is formed, organic molecules can then be assembled between the metal leads forming a nanojunction. The third approach involves the deposition (or self-assembly) of an organic thin film onto a metal substrate before the introduction of a second conducting lead, which may be a metal thin film by vapor deposition, a conventional electrode, or a conducting scanning probe (6, 37, 38). In such a configuration, depending on the dimensions of the second lead electrode, one can evaluate the charge transport of a single molecule or an ensemble.

Regardless of the preparation methods of the molecular junctions, the chemical nature of the interfacial contacts between the metal electrodes and the organic molecules/layers has been found to significantly impact the charge transport across nanojunctions (6). Schottky contacts on wide-band-gap materials often exhibit significant device-to-device variations and nonideal behaviors in current-voltage (I-V) measurements, whereas with ohmic contacts at the interface, charge transport across the junctions is facilitated.

In an early study, Lindsay and coworkers (39) developed a reliable technique to measure the conductivity properties of single molecules in which they inserted molecules of 1,8-octanethiol dithiol into a 1-octanethiol self-assembled monolayer (SAM) on an Au(111) surface by a replacement reaction. The low concentration of the dithiol molecules made it possible to isolate one from another and hence to examine the transport properties at the single-molecule level. Gold colloidal nanoparticles were then anchored onto the terminal thiols, and a junction was created by using a gold-coated conducting atomic force microscope (AFM) tip to locate and contact the gold nanoparticles (Figure 1a). As highlighted by the I-V curves in Figure 1, transport measurements showed that the junction conductance varied statistically as multiples of a fundamental curve ascribed to assemblies in which a single dithiol molecule linked the gold nanoparticle to the underlying gold substrate. From these studies, the resistance of a single octanethiol molecule was estimated to be 900 ± 50 MΩ—for comparison, the electrical resistance of a single α,α'-xylyldithiol (XYL) molecule was estimated to be ∼18 ± 12 MΩ, based on coulomb staircase studies of gold nanoparticles immobilized onto the XYL dithiol self-assembled monolayer surfaces (25). Additionally, the junction conductance through bonded contacts was at least four orders of magnitude greater than that of nonbonded contacts (i.e., through the methyl terminus), along with a different voltage dependence.

In another study, Engelkes et al. (40) prepared nanoscale tunnel junctions by contacting gold-, platinum-, or silver-coated AFM tips to SAMs of alkanethiol or alkanedithiol molecules on polycrystalline gold, platinum, or silver substrates (Figure 2). For alkanedithiol monolayers (Figure 3b), the sigmoidal I-V profiles exhibited symmetrical characters, suggesting similar bonding contacts at both molecular termini, whereas for alkanethiol monolayers (Figure 3a), slightly more currents were observed when the tip was biased negatively relative to the substrate. Importantly, the I-V curves can be fitted by the Simmons equation for tunneling through a square barrier, where $A$ is the junction area, $s$ is the width of the barrier, $m$ is the electron mass, and $\phi$ is the barrier height (41). At low biases, the equation can be simplified as

$$ R = R_0 \exp(\beta n) $$

where $R$ is the junction resistance (V/I), $R_0$ is the effective contact resistance, $\beta$ is the structure-dependent attenuation factor, and $n$ is the number of repeat units of the alkyl spacer. According to Schottky contacts: exhibit rectified charge transport with a barrier ($>kT$) defined by the metal Fermi energy and the semiconductor band edge.
Figure 1

(a, inset) Schematic representation of the experiment. The sulfur atoms (red dots) of octanethiols bind to a sheet of gold atoms (yellow dots), and the octyl chains (black dots) form a monolayer. The second sulfur atom of a 1,8-octanedithiol molecule inserted into the monolayer binds to a gold nanoparticle, which in turn is contacted by the gold tip of the conducting atomic force microscope (AFM). Illustrated in the main panel are $I(V)$ curves measured with the apparatus diagrammed in the inset. The five curves shown are representative of distinct families, $N I(V)$, that are integer multiples of a fundamental curve, $I(V)$ ($N = 1, 2, 3, 4, \text{ and } 5$). (b) Curves from panel a divided by 1, 2, 3, 4, and 5. (c) Histogram of values of a divisor, $X$ (a continuous parameter), chosen to minimize the variance between any one curve and the fundamental curve, $I(V)$. It is sharply peaked at integer values 1.00 ± 0.07 (1,256 curves), 2.00 ± 0.14 (932 curves), 3.00 ± 0.10 (1,002 curves), 4.00 ± 0.10 (993 curves), and 5.00 ± 0.10 (993 curves). (Spreads are ±1 standard deviation.) Of 4,579 randomly chosen curves, over 25% correspond to the $X = 1$ (single-molecule) peak. No obvious correlation was noted between particle size and the number of molecules contacted. Conducting AFM data were acquired with a PicoSPM microscope (Molecular Imaging) using silicon cantilevers (spring constant, 0.35 N m$^{-1}$) sputter-coated with 5 nm of chromium followed by 50 nm of gold. Imaging was done under toluene in a nitrogen atmosphere. Figure reproduced by permission from Reference 39, copyright (2001) American Association for the Advancement of Science.

Figure 4 depicts the semilog plots of the variation of the junction resistance with the alkyl chain length, which exhibit a clear exponential correlation. From linear regression of the experimental data, $R_0$ and $\beta$ can be quantitatively evaluated from the intercept and slope, respectively. There are at least three aspects that warrant attention here. First, the $\beta$ coefficients are the same for both the alkanethiol and alkanedithiol monolayers, suggesting the same scaling of the film thickness with chain length. Second, the contact resistance is one to two orders of magnitude lower with the doubly bound alkanedithiol junctions than with the singly bound alkanethiol ones. Third,
the contact resistance decreases with increasing work function of the metal electrodes, Ag < Au < Pt, as shown in Figure 5, which is accounted for by hole transport across the junction as the Fermi level is nearer the HOMO* than the LUMO*.

The impacts of interfacial contacts on charge transport have also been observed in molecular junctions with macroscopic electrodes. For instance, Slowinski and coworkers (46) employed two mercury electrodes to examine the tunneling resistance of monolayers and bilayers of $n$-alkanethiols. There are two junction configurations: one with the two mercury electrodes modified with a SAM of alkanethiols and the other with the alkanethiol monolayers adsorbed only on one mercury electrode. The authors then brought the two electrodes into contact,
forming a macroscopic junction, with a structure of Hg-S-(CH₂)ₙ-CH₃|CH₃-(CH₂)ₙ-S-Hg and Hg-S-(CH₂)ₙ-CH₃|Hg, respectively. For both monolayer and bilayer junctions, the tunneling currents decreased exponentially with the junction width defined by the monolayer/bilayer thickness, and a tunneling coefficient \( \beta = 1/CH₂ \). Yet the tunneling current of the monolayer junctions was at least an order of magnitude smaller than that of the bilayer junctions containing the same number of carbon atoms across the junction. For instance, the authors reported that the tunneling current recorded for a monolayer of \( n \)-octadecanethiol was approximately 2.0 ± 0.5-fold smaller than that for a bilayer of \( n \)-nonanethiol, although the geometric thickness of the latter junction was greater than that of the former. This was accounted for by the inefficient electronic coupling at the -CH₃|Hg interface as compared with that at the -CH₃|CH₃- interface, although both were nonbonding in nature (47).

Further enhancement of the junction charge transport can be achieved by covalent linking at the interface between the two SAMs (in bilayer junctions). This was highlighted by Whitesides and coworkers (48), who prepared two types of bilayer junctions (Figure 6). The first (Figure 6b) involves SAMs of simple \( n \)-alkanethiols on a mercury electrode and on another metal electrode.
The HDT-covered mercury drop (C16-Hg) was then brought into contact with the solid electrode using a micromanipulator. The area solution of hexadecanethiol (HDT) from a capillary connected to a mercury reservoir, and a SAM of HDT was allowed to form on it. Anhydride, $Y=\text{CO}_2\text{H}$ and $Y=\text{HO}_2\text{C}$, or $X=\text{CO}_2\text{H}$ and $Y=\text{H}_2\text{N}$ or interact strongly but noncovalently ($X=\text{CO}_2\text{H}$ and $Y=\text{HO}_2\text{C}$, or $X=\text{CO}_2\text{H}$ and $Y=\text{H}_2\text{N}$) through hydrogen or ionic bonds. Figure reproduced with permission from Reference 48, copyright (2001) John Wiley and Sons.

In the above studies, the organic molecules are assembled onto the electrode surface largely by metal-thiolate bonds. In fact, mercapto derivatives have been used as the molecules of choice in the formation of stable molecular assemblies on metal surfaces by virtue of the strong affinity of thiol moieties to transition metals (49). However, recent studies demonstrate that with an interfacial contact of metal-carbon covalent bonds, the interfacial contact resistance may be reduced markedly, leading to further improvement of the junction charge transport. For instance, Cheng et al. (50) used trimethyl tin (SnMe$_3$)-terminated polymethylene chains to form single-molecule junctions with a break junction technique (Figure 8). Au-C bonds were formed by the displacement of the SnMe$_3$ moieties by gold atoms at the electrode surface. The resulting junctions showed a conductance that was $\sim$100 times larger than that with analogous alkanes with most other terminations (e.g., $-\text{NH}_2$), which was ascribed to the formation of Au-C $\sigma$ bonds. Studies with a variation of the alkane chain length showed that the tunneling currents decreased exponentially with molecular length, with a decay constant ($\beta$) of 0.97 per CH$_2$ (46), suggesting a nonresonant...
Figure 7
Plots of current density as a function of the bias voltage between mercury and gold electrodes for junctions Au-SAM(1)-X~Y-SAM(7)-Hg. The error bar is plus or minus the standard deviation of the data. The symbols X and Y denote terminal functional groups of the monolayers, the double lines represent a van der Waals contact, the three middle dots are for hydrogen bonding, and the single line is for covalent bonding. Figure reproduced with permission from Reference 48, copyright (2001) John Wiley and Sons.

transport mechanism, similar to conventional junctions based on metal-thiolate linkages (49).

Using the same junction configuration, further studies with \( \pi \)-conjugated molecules demonstrated enhanced electronic coupling between the metal electrode and the \( \pi \) system (Figure 9) (51). For instance, the junctions formed with the prototypical example of 1,4-dimethylenebenzene showed a conductance approaching one conductance quantum (\( G_0 = 2e^2/h \)), and for longer oligophenyl-based junctions, the charge transport was tunneling in nature. Furthermore, calculations based on density functional theory (DFT) showed that for the Au-xylene-Au junction, near-resonant transmission was likely, with a crossover to tunneling for the longer oligomers.

Furthermore, using junctions with organic molecules sandwiched between a mercury electrode and highly doped silicon, Yaffe et al. (52) found that the substitution of an alkyl monolayer with an alkenyl one on the Si(111) surface further facilitated the junction charge transport, with the double bonds enhancing the coupling between the organic monolayers and the silicon substrate. In fact, theoretical studies based on DFT showed that the silicon-related states extended further into the molecular region in the alkenyl ligands (up to the third carbon) than in the alkyl case (up to the second carbon). Experimentally, this was manifested by an increase of the junction current density at a given bias as a result of the increasing contact conductance, i.e., \( (4.7 \pm 1.3) \times 10^{-7} \) \( G_0 \) for alkyl and \( (13 \pm 8) \times 10^{-7} \) \( G_0 \) for alkenyl monolayers.

The examples cited above clearly demonstrate that interfacial resistance may be reduced significantly by switching nonbonding contacts with bonding ones, and of the interfacial bonding interactions, metal-carbon covalent bonds are more effective in electronic coupling between the molecules and the electrode than metal-thiolate bonds. Furthermore, the hybridization state of the anchoring carbon is critical in manipulating the interfacial electronic coupling and hence the charge transport of a molecular junction. In fact, metal-carbon bonding interactions have been recognized to impact charge-transport characteristics in nanoelectronic devices based on carbon nanotubes or graphene, in which metal leads are generally deposited onto the carbon nanostructures to make electrical contacts (53). A series of theoretical studies (54–56) demonstrated that in addition to metal work functions, the chemical nature of the interfacial bonding interactions also plays a significant role in determining the height of the Schottky barrier.
Figure 8

Conductance data for SnMe3-linked alkanes. (a) Junction formation and conductance measurements with 1,4-bis(trimethylstannyl)butane molecules between gold electrodes. Hydrogen atoms are shown in white, carbon atoms in gray, and tin atoms in green. (b) Sample traces showing conductance on a logarithmic scale versus relative displacement for SnMe3-terminated alkanes with four (C4, red), six (C6, blue), eight (C8, green), and ten (C10, orange) methylene groups in the backbone. (c) Conductance histograms for C4, C6, C8, C10, and C12. Each histogram is constructed from 10,000 traces and is generated without any data selection. Bin size is $10^{-4}G_0$ for C4, $10^{-5}G_0$ for C6 and C8, $10^{-6}G_0$ for C10, and $10^{-7}G_0$ for C12. Upward arrows indicate primary conductance peaks; downward arrows indicate lower conducting shoulders. Asterisks indicate conductance peaks due to the dimer molecule formed in situ. (d) Conductance at the peak on a logarithmic scale versus the number of methylene groups in the backbone for SnMe3-terminated alkanes (red) and diamine-terminated alkanes (blue). Figure reproduced with permission from Reference 50, copyright (2011) Nature Publishing.

These fundamental insights may account for the wide disparity of the contact resistance between carbon nanotubes and metal leads. For instance, an ohmic contact between silver and amorphous carbon nanotubes was observed with arrays of one-dimensional heterostructures fabricated by combining electrochemical deposition and chemical vapor deposition with porous membranes as the templates (57). Nihei and coworkers (58) grew multiwall carbon nanotubes with a nickel catalyst layer on a titanium electrode surface by hot-filament chemical vapor deposition and found that the contact resistance with the nickel/titanium electrode was two orders of magnitude lower.

**Ohmic contact:** a nonrectifying junction with a linear and symmetrical current-potential profile.
than that without the titanium substrate. This was ascribed to the formation of titanium carbide during nanotube growth and the end bonding configuration of the nanotubes on titanium. In a study based on the first-principles quantum mechanical density functional and matrix Green’s function methods, Matsuda et al. (59) examined the I-V characteristics and contact resistance of end- and side-contacted metal-carbon nanotube and metal-graphene interfaces with five different metals (titanium, palladium, platinum, copper, and gold). They observed that in the end-contacted configuration, the contact resistance (normalized to surface carbon atoms) was 107 kΩ for titanium, 142 kΩ for palladium, 149 kΩ for platinum, 253 kΩ for copper, and 187 kΩ for gold, whereas in the side-contacted configuration, it was markedly higher, at 8.6 MΩ for palladium, 34.7 MΩ for platinum, and 630 MΩ for copper.

These results strongly suggest that end contact between a carbon nanotube or graphene and a metal is most effective in reducing the interfacial contact resistance, likely a result of the formation of more extensive chemical bonding at the interface. In addition, among the metals investigated, palladium appears to be the optimal choice in wetting carbon nanotubes and graphene, leading to an improved diminishment of the contact resistance (60–63). This is consistent with results observed with metal nanoparticles passivated by metal-carbon covalent bonds, as detailed below. However, the nature of the interfacial bonds (e.g., single bonds, double bonds) involving carbon nanotubes or graphene has remained largely unresolved in experimental measurements. Breakthroughs toward this end are urgently needed so that the performance of nanoelectronic devices based on these carbon nanostructures may be further improved and optimized (64).

3. ORGANICALLY CAPPED NANO Particles

That direct bonding interactions between metals and carbon nanotubes lead to a drastic decrease in the interfacial contact resistance may be exploited for the manipulation of nanoparticle optical and electronic properties by passivating the nanoparticles with metal-carbon covalent bonds. This has been demonstrated recently in a series of studies. In this section, we highlight some recent progress in the functionalization of metal nanoparticles with metal-carbon covalent bonds and the impacts of these unique interfacial bonding interactions on nanoparticle charge-transfer chemistry in comparison with the metal-thiolate ones.

4.1. Metal-Carbon Bonds

In most earlier studies, alkanethiols and other thiol derivatives were used extensively as the ligands of choice to stabilize metal nanoparticles by taking advantage of the strong affinity of thiol groups to transition-metal surfaces (65–69). Yet because of the lack of interesting chemistry of
the metal-sulfur bonds, the impacts of the metal-ligand interfacial bonding interactions on the nanoparticle material properties have been largely ignored. For instance, in studies of nanoparticle electronic conductivity, the predominant energetic barrier to interparticle charge transport is generally assumed to result from the organic capping ligands that intercalate between adjacent particles (70–73). Yet with the variation of the metal leads as well as that of the chemical structure of the molecular linkers (including metal-anchoring groups), one may envision that the energetic landscape for charge transport will be readily manipulated. For instance, diazonium derivatives have been used rather extensively for the functional grafting of a variety of transition-metal surfaces by virtue of the formation of a metal-carbon covalent bond. Theoretical studies based on DFT calculations (74) have shown that the energy for the chemisorption of aryl moieties onto metal surfaces (e.g., titanium, iron, copper, silver, palladium, and gold) by diazonium precursors decreases from left to right in the periodic table with the increasing number of d electrons. They correlated this changing trend with the center of the metal d band, which shifts further below the Fermi level with an increasing number of d electrons, thus effectively weakening the bonding between the metal surfaces and the aryl adsorbates. Importantly, this study also suggests that the adsorbates may adopt two surface configurations: an upright orientation in favor of a metal-carbon σ bond, which is anticipated with transition metals to the right of iron in the periodic table, and a tilted/flat arrangement to favor a metal-carbon π bond with transition metals to the left of iron in the periodic table. One can therefore envision that the metal-carbon contact resistance may be systematically varied by the deliberate selection of transition-metal substrates.

These theoretical insights provide a fundamental basis on which nanoparticle charge-transfer dynamics may be further manipulated. In fact, reports of transition-metal nanoparticles protected by metal-carbon covalent bonds have recently started to appear, allowing nanoparticle optoelectronic properties to be examined and compared within the context of metal-ligand interfacial contacts. Of these, the enhanced metal-ligand bonding interactions as a consequence of metal-carbon covalent bonds are anticipated to lead to extended spilling of the nanoparticle core electrons into the organic protecting matrix, and hence enhanced interparticle charge transfer (75–80).

In a recent study, Mirkhalaf et al. (75) used aryl diazonium derivatives as both the phase-transfer reagents and precursors for nanoparticle surface stabilization to prepare platinum (3 ± 1-nm diameter) and gold (8.0 ± 0.8-nm diameter) nanoparticles capped with metal-carbon covalent linkages (Figure 10) (75). Surface-enhanced Raman spectroscopic measurements (79) showed that the Pt-C vibrational band likely appeared within the range 410–420 cm$^{-1}$. The procedure was also adopted to prepare palladium (76), ruthenium (80), and titanium (77) nanoparticles capped with various aryl derivatives by metal-carbon bonds. The resulting nanoparticles exhibited electronic

![Figure 10](image-url)
conductivity that was markedly greater than that of the mercapto-passivated counterparts. For instance, biphenyl-capped palladium (Pd-BP) nanoparticles were prepared using 4-biphenyl diazonium as the precursor, with an average core diameter of $3.6 \pm 0.8 \text{ nm}$, and the electronic conductivity was measured at controlled temperatures at which the nanoparticles were deposited onto an interdigitated array electrode. The I-V profiles exhibited a rather interesting dependence on temperature. Figure 11a shows the I-V curves of the Pd-BP nanoparticles within the temperature range 80–300 K. The I-V responses exhibit a linear (ohmic) character within the entire temperature range under study, suggesting efficient interparticle charge transfer. This is not surprising, considering the short and aromatic capping layer. As compared to control measurements with the same blank electrode (current of the order of picoamperes), the currents of the particle solid films are significantly greater, of the order of milliamperes, even at a potential bias of only $\pm 0.4 \text{ V}$. More importantly, the currents are found to decrease with increasing temperature (80 K to 320 K), a behavior actually anticipated for metallic materials (81). From the slope of the I-V curves, one can calculate the conductivity of the particle solid films, which is of the order of $10^{-2} \text{ S m}^{-1}$ (Figure 11b). This is about nine orders of magnitude smaller than that of bulk palladium [approximately $0.93 \times 10^{7} \text{ S m}^{-1}$ at room temperature (81)], which can be ascribed to the metal-organic nanocomposite nature of the particles. Additionally, the particle conductivity decreases (almost linearly) with temperature in the range 80–300 K (Figure 11b). Although the decrease is less dramatic than that of the bulk metal, the observation deviates significantly from previous studies of metal nanoparticles protected with arylthiol derivatives in which the conductivity is generally found to increase with increasing temperature (73, 82–85); namely, the particle ensembles behave as semiconductor materials.

As the average core diameter of Pd-BP nanoparticles is $\sim 3 \text{ nm}$, the particle cores will behave similarly to bulk palladium. Thus the ensemble conductivity is anticipated to be mainly determined by the palladium-ligand contact and the ligand matrix itself. Yet, as mentioned above, palladium has extensively been used as the metal of choice to create contacts with carbon nanotubes because of strong Pd-C bonding interactions and low contact resistance (60–62). Furthermore, the $\pi-\pi$ stacking as a result of ligand intercalations between adjacent particles in the solid films may serve...
as an effective pathway for interparticle charge transfer (86). Hence it is most probable that the combination of these factors gives rise to the metal-like conductivity properties of Pd-BP particle solids.

The introduction of a saturated spacer into the capping ligands causes the resulting particles to exhibit drastic differences in I-V measurements. Figure 12a,b depicts the I-V data of decylphenyl-
stabilized palladium (Pd-DP) particles prepared in a similar fashion. The linear I-V profiles can also be seen within the entire temperature range of 80–320 K (Figure 12), but the magnitude of the currents (of the order of tens of nanoamperes) is substantially smaller than that observed with Pd-BP particles (Figure 11), although it is still significantly larger than that of the background currents. This can be ascribed to the long decyl spacer that impedes interparticle charge transfer.

In contrast to the Pd-BP particles, which exhibit a monotonic decrease in ensemble conductivity with increasing temperature (Figure 11), the behaviors of Pd-DP particles are somewhat more complicated. From Figure 12a, one can see that the current first increases with increasing temperature from 80 to 180 K, exhibiting semiconductor characters, yet with a further increase in temperature (from 180 to 320 K), the current actually starts to decrease (Figure 12b), akin to that observed in Figure 11 in which the particle films behave instead like metallic materials. Figure 12c summarizes the ensemble conductivity with temperature and clearly depicts a transition temperature at approximately 180 K at which the interparticle charge transfer evolves from semiconductor to metallic behaviors.

These unique charge-transfer behaviors were also observed with ruthenium (80) and titanium (77) nanoparticles capped by similar aryl fragments. In sharp contrast, for (even slightly larger) palladium nanoparticles passivated by mercapto derivatives, the corresponding I-V profiles exhibited only semiconducting characters within the same range of temperature (87).

However, such a semiconductor-metal transition is not limited to nanoparticles capped with metal-carbon bonds. In a previous study of the resistivity of monolayers of much larger silver nanoparticles (7.8-nm diameter) passivated by octanethiolates or decanethiolates (88), the films exhibit a metal-like resistance at temperatures above 200 K, whereas at lower temperatures (60 to 200 K), the films behave as a semiconductor. In another study, Snow & Wohltjen (84) measured the conductance of solid films of dodecanethiolate-stabilized gold nanoparticles of varied sizes. For particles with a core diameter less than 5.0 nm, the authors observed only a semiconductor-like temperature dependence of the ensemble conductivity within the temperature range 190–300 K. For larger particles (core diameters of approximately 6.0 nm and 7.2 nm), the ensemble conductivity evolved from semiconducting to metallic behaviors with increasing temperature, and the transition temperature decreased with increasing particle core size, from 260 K (6.0 nm) to 240 K (7.2 nm). More recently, Murray and colleagues (89) reported that temperature-induced core motion could also lead to a drastic enhancement of the ensemble conductivity as a consequence of the thermal modulation of interparticle separations.

Taken together, the above observations can be rationalized by Mott’s model for the metal-insulator transition (90). According to this model, a compressed lattice of hydrogen atoms is anticipated to exhibit metallic behaviors when the interatomic distance approaches $\sim 4.5a_0$, where $a_0$ is the Bohr radius. By approximating nanoparticles as artificial atoms, one obtains $a_0 : \frac{\hbar}{\sqrt{2m^*\phi}}$, where $m^*$ is the effective mass of the electrons, $\phi$ is the barrier height, and $\hbar$ is Planck’s constant. Thus the transition of the conductance of a nanoparticle ensemble into the metallic domain only occurs when the interparticle charge transfer is sufficiently enhanced. This can be achieved by increasing the particle core size (thus lowering the coulombic barrier for interparticle charge transfer), decreasing the particle-ligand contact resistance (hence enhancing electronic spilling beyond the metal cores), and raising the ensemble temperature (by virtue of thermal activation and core thermal motions). Thus, whereas the above-mentioned Pd-DP particles are substantially smaller than the Au-SR (84) and Ag-SR (88) particles that exhibit similar semiconductor-metal transitions with increasing temperature, the Pd-DP particles benefit from the strong Pd-C bonding and hence the markedly reduced interfacial contact resistance that offset the core size effects.
3.2. Metal-Carbene Bonds

More complicated metal-ligand interfacial bonding interactions have also been achieved using diazo ligands as the precursors, which are self-assembled onto metal nanoparticle surfaces forming metal-carbene π bonds and concurrently releasing nitrogen (91, 92). The conjugated interfacial bonds endow two unique properties to the nanoparticles. The first is that the nanoparticles may be further functionalized by olefin metathesis reactions with vinyl derivatives, and the other is that extended conjugation may emerge between particle-bound functional moieties, for which effective intraparticle charge delocalization may occur, leading to the appearance of unprecedented optical and electronic properties of the nanoparticle materials. This is drastically different from those described in Section 3.1 with metal-carbon single bonds. For instance, nanoparticle-mediated intervalence transfer was reported with ferrocene moieties that were attached onto the ruthenium nanoparticle surface by ruthenium-carbene π bonds using vinylferrocene as the illustrating example, Ru = CH-Fc (Figure 13) (93). The resulting particles exhibited two pairs of voltammetric waves with a potential spacing of approximately 200 mV (Figure 14), arising from the redox reactions of particle-bound ferrocene, Fc⁺ + e ↔ Fc, and a rather intense absorption peak in the near-infrared range (∼1,930 nm) at mixed valence. Both features were consistent with those of dimeric ferrocene with a conjugated chemical bridge and suggested class II characteristics of the intraparticle intervalence transfer that mainly arose from through-bond interactions between the metal centers (94). Quantum calculations based on DFT showed that the nanoparticle core electrons served as conducting band states for the effective charge delocalization between particle-bound ferrocene moieties. In contrast, when the nanoparticles were functionalized with allylferrocene in which an sp³ carbon was inserted into the interfacial bridge (Ru = CH-CH₂-Fc), the electronic communication diminished drastically, leading to the appearance of only one pair of voltammetric waves, analogous to monomeric ferrocene (95). Similar behaviors were observed when the ferrocene moieties were bound onto a (macroscopic) metal electrode surface by similar ruthenium-carbene π bonds (96). These studies provide a first direct verification of Hush’s (97) hypothesis made more than four decades ago that effective electronic communication might take place when redox-active moieties are anchored onto an electrode surface by a conjugated linker.

When fluorophores [e.g., pyrene (98) and anthracene (99)] are bound onto the nanoparticle surface by similarly conjugated metal-ligand bonds, the nanoparticles exhibit optical properties that are consistent with those of their dimeric derivatives. For instance, in a recent study, we prepared ruthenium nanoparticles functionalized with pyrene moieties by olefin metathesis re-

Figure 13
Olefin metathesis reaction of carbene-functionalized nanoparticles. Figure reproduced with permission from Reference 93, copyright (2008) American Chemical Society.
actions of carbene-stabilized nanoparticles with 1-vinylpyrene and 1-allylpyrene (referred to as Ru = VPy and Ru = APy, respectively) (98). In fluorescence measurements, Ru = VPy nanoparticles exhibited two prominent emission bands at 392 nm and 490 nm, similar to those of \((E)\)-1,2-di(pyren-1-yl)ethene, suggesting that the particle-bound pyrene moieties behave equivalently to pyrene dimers with a conjugated linker by virtue of the ruthenium-carbene \(\pi\) bonds. In sharp contrast, Ru = APy nanoparticles displayed only a single emission peak at 392 nm, consistent with monomeric pyrene derivatives of 1-vinylpyrene and 1-allylpyrene. This again implies that the intraparticle extended conjugation was effectively turned off by the insertion of an \(sp^3\) carbon into the chemical linker that bound the pyrene moieties onto the nanoparticles.

### 3.3. Metal-Alkynide Bonds

Recently we also functionalized ruthenium nanoparticles with 1-octynyl fragments by the formation of Ru-C≡ interfacial bonds (Figure 15) (100). Experimentally, 1-octyne first reacted with \(n\)-butyl lithium to produce 1-octynide lithium, which was then added into a solution of RuCl₃.
Reduction by superhydride led to the production of octynide-protected ruthenium nanoparticles. Transmission electron microscopic measurements showed that the resulting particles exhibited an average core diameter of $2.55 \pm 0.15$ nm with well-defined ruthenium crystalline lattice fringes. Because of the formation of Ru-C≡ interfacial bonds, the C≡C vibrational stretch in Fourier transform infrared (FTIR) measurements red-shifted to 1,936 cm$^{-1}$ from 2,119 cm$^{-1}$ that was observed for monomeric 1-octyne. Interestingly, the nanoparticles underwent ligand exchange reactions with alkynyl lithium (e.g., 5-phenyl-1-pentylnyl lithium) for further surface functionalization (Figure 15), as manifested in FTIR as well as $^1$H and $^{13}$C NMR measurements. Optically, whereas ultraviolet-visible absorption measurements exhibited only a featureless profile, the ruthenium nanoparticles displayed apparent photoluminescence with an emission peak at 428 nm, which was accounted for by intraparticle charge delocalization as a consequence of the strong Ru-C≡ interfacial bonds and the conducting ruthenium metal cores such that the particle-bound C≡C moieties behaved analogously to diacetylene (-C≡C-C≡C-) derivatives. The impacts of the interfacial bonding interactions on intraparticle charge delocalization were further illustrated by ruthenium nanoparticles functionalized with a mixed monolayer of both octynyl and ethynylferrocene ligands. At a ferrocene surface coverage of approximately 13%, electrochemical measurements depicted two pairs of voltammetric peaks with a potential spacing of 265 mV. A new near-infrared absorption band centered at approximately 1,687 nm also started to emerge with the addition of nitrosonium tetrafluoroborate (NOBF$_4$) as the oxidizing reagent, and the peak intensity exhibited a volcano-shape dependence on the amount of NOBF$_4$ added. These observations strongly suggest an effective intervalence charge transfer between the particle-bound ferrocene groups at mixed valence, analogous to the observation of ferrocene moieties bound onto the particle surface by ruthenium-carbene $\pi$ bonds (93). Yet the larger potential spacing between the two voltammetric peaks and the higher energy of the near-infrared absorption peak indicate that the conjugation between the particle-bound ferrocenyl moieties appeared to be stronger with the Ru-C≡ bonds than with the Ru = C bonds.

### 3.4. Ruthenium-Vinylidene Bonds

In a more recent study, Kang et al (101) stabilized ruthenium nanoparticles by the self-assembly of 1-alkynes onto the bare ruthenium colloid surface (Figure 16). The formation of a ruthenium-vinylidene (Ru = C = CH-R) interfacial bonding linkage was confirmed by the specific reactivity of the nanoparticles with imine derivatives forming a heterocyclic complex at the metal-ligand interface, as manifested in $^1$H and $^{13}$C NMR, photoluminescence, and electrochemical measurements in which a ferrocenyl imine was used as the labeling probe. Notably, the resulting nanoparticles could also undergo olefin metathesis reactions with vinyl-terminated molecules, as exemplified by the functionalization of the nanoparticles with 1-vinylpyrene (98). In sharp contrast, no reactivity was observed with 1-dodecynide-stabilized ruthenium nanoparticles with either imine or vinyl derivatives because these (deprotonated) nanoparticles were stabilized instead by the formation of a Ru-C≡ $\pi$ bond at the metal-ligand interface.

With this unique interfacial bond, the nanoparticles exhibit interesting electronic conductivity properties with linear I-V curves within the potential range of $-0.8 \text{ V}$ to $+0.8 \text{ V}$ at varied temperatures (200–300 K) (102). The ohmic characters were partly ascribed to the spilling of core electrons into the organic capping layer that facilitated interparticle charge transfer (vide ante; see Section 3.1). Furthermore, studies of the nanoparticle electronic conductivity showed that the coupling coefficient ($\beta$) was approximately 0.31 Å$^{-1}$ for nanoparticles stabilized by short-chain alkynes (1-hexyne, 1-octyne, and 1-decylene) and 1.44 Å$^{-1}$ for those with long-chain alkynes, such as 1-dodecyne, 1-tetradecyne, and 1-hexadecyne. This may be accounted for by the relative
contributions of the conjugated metal-ligand interfacial bonding interactions versus the saturated aliphatic backbones of the alkyne ligands to the control of interparticle charge transfer.

3.5. Manipulation of Intraparticle Charge Delocalization

As mentioned above, intraparticle charge delocalization is facilitated by conjugated metal-ligand bonding interactions as well as the conducting metal cores (93). Thus the manipulation of the core valence state is anticipated to impact the electronic communication between nanoparticle-bound functional moieties. Using 1-octynide-stabilized ruthenium nanoparticles as the illustrating example, Kang et al. (103) demonstrated that intraparticle charge delocalization can be readily manipulated by the nanoparticle charge state, which was achieved by chemical reduction or oxidation. This is in sharp contrast to earlier work with gold nanoparticles passivated by thiol derivatives in which the impacts of the depletion or injection of core free electrons were essentially confined to metallic cores (104). For instance, for nanoparticles with a net gain (loss) of 0.6 electron per particle by NaBH₄ reduction [Ce(SO₄)₂ oxidation], the bonding order of the particle-bound C≡C moieties exhibited an apparent decrease (enhancement), as manifested in FTIR and X-ray photoelectron spectroscopy measurements. This suggests that the extended conjugation between the particle-bound C≡C moieties became strengthened (weakened) when the nanoparticles were charged (discharged), which may result from the nanoparticle metallic cores serving as the conducting media to facilitate intraparticle charge delocalization. As a result, the nanoparticle photoluminescence characteristics vary accordingly. Whereas the peak position of the emission profiles exhibits only a slight variation, the intensity of the reduced nanoparticles was markedly enhanced and that of the oxidized nanoparticles exhibited an apparent suppression, in comparison to the as-prepared nanoparticles. These results demonstrate that nanoparticle optoelectronic properties may be further manipulated by the nanoparticle charge state, by taking advantage of the molecular capacitor characters of the particles as well as the strong metal-ligand interfacial bonding interactions.
Further studies show that electrostatic polarization of the nanoparticle core electrons by the selective binding of metal cations to the particle-bound functional moieties also leads to an apparent variation of the nanoparticle-mediated electronic communication (105, 106). This behavior may be exploited for chemical sensing applications.

4. SUMMARY AND PERSPECTIVES

In this review article, we highlight some recent studies on the fundamental significance of metal-organic contacts in the manipulation of the dynamics of interfacial charge transfer, a critical process in molecular and nanoscale electronics. Whereas most studies have been confined to interfaces with metal-thiolate bonds, recent studies have shown that metal-carbon covalent bonds may also be formed at the metal-ligand interface, which exhibit markedly reduced interfacial resistance in comparison with the corresponding metal-thiolate counterparts. As such, the energetic barrier in charge transport across molecular junctions may be reduced significantly. Furthermore, for organically capped nanoparticles, the conjugated nature of the interfacial linkages leads to effective intraparticle charge delocalization and hence enhanced charge transport between neighboring nanoparticles.

Within this context, one may ask what other metal-nonmetal bonds are possible in the fabrication of molecular junctions or functionalization of nanoparticles. We note that in addition to metal-carbon bonds, a wide variety of metal-nonmetal bonds has been rather extensively observed in organometallic chemistry, such as metal-nitrogen and metal-silicon bonds. Of these, metal-nitrene (M=N) bonds have been proposed or recognized in a variety of organometallic complexes that are involved in bond-activation reactions (e.g., C-H bond activation, nitrene-exchange or nitrene-transfer reactions), in which the unique reactivity is attributed to the high polarizability of the M=N bonds (107–109). It is generally believed that the nitrene group is stabilized by the \(\sigma\pi\) (metal) \(\rightarrow\) \(\pi\pi\) (nitrene) back-bonding interactions that involve both \(\sigma\) and \(\pi\) components (110, 111). In addition, metal-silicon bonds have been formed with a variety of transition metals (112–115). An understanding of the chemical nature and reactivity of the metal-silicon bonds (116–118) is anticipated to shed light on the formation and manipulation of the energetic barrier for interfacial charge transport in silicon-based semiconductor devices, for which metal-silicon contacts are an essential component (119).

Yet it remains a challenge to develop effective procedures to create reliable metal-nitrogen or metal-silicon bonds at molecular junctions or on metal nanoparticle surfaces (120). This is limited primarily by the lack of appropriate organic functional moieties. Thus the rational design and synthesis of unique organic ligands represent critical first steps in unraveling the mechanistic insights of the impacts of these interfacial bonding contacts on the charge-transport dynamics involved. It is envisaged that the rich reactivity of these metal-ligand bonds, as manifested in diverse organometallic complexes, may be exploited as a unique platform for further and more deliberate functionalization and engineering of molecular and nanoscale electronic assemblies and devices.

**SUMMARY POINTS**

1. Charge transfer through bonded contacts is more efficient than that through nonbonded contacts, suggesting that the energetic barrier for through-bond transfer is lower than that for through-space transfer.

2. Interfacial contact resistance may be diminished drastically with metal-carbon covalent linkages, as compared with the metal-thiolate ones, for which the work functions of the metal substrates also play an important role.
3. For conjugated metal-carbon linkages, effective electronic communication may occur between functional moieties bound onto metal electrode or nanoparticle surfaces.

4. More diverse metal-ligand interfacial bonding interactions may be achieved by a rational design and synthesis of unique functional ligands.

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93. Presents the first observation of electronic communication between nanoparticle-bound functional moieties through conjugated metal-ligand interfacial bonds.

94. Reviews organometallic complexes that exhibit intervalence transfer and their classification based on the extent of electronic interactions.

101. Identifies the formation of ruthenium-vinylidene interfacial bonds upon the self-assembly of 1-alkynes on ruthenium nanoparticle surfaces.


