

## Looking Ahead: Challenges and Opportunities in Organometallic Chemistry<sup>†</sup>

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Some of the possible roles that organometallic chemistry will play in the future are discussed and reflected upon against the backdrop of current global uncertainty. In particular, the manipulation of organometallic excited states, redox states, and magnetic properties for use in energy generation, photocatalysis, and molecular electronics is discussed.

### Introduction

Dicebat Bernardus Carnotensis nos esse quasi nanos, gigantium humeris insidentes, ut possimus plura eis et remotiora videre, non utique proprii visus acumine, aut eminentia corporis, sed quia in altum subvenimur et extollimur magnitudine gigantean.

As Bernard of Chartres has said “we are like dwarfs on the shoulders of giants, so that we can see more than they, and things at a greater distance, not by virtue of any sharpness of sight on our part, or any physical distinction, but because we are carried high and raised up by their giant size.”

John of Salisbury

An invitation to write about what future directions might be taken in any discipline brings considerable excitement from the freedom to range over the expanse of what we know and to ponder on what we do not. It is perhaps more burdensome to consider where the responsibility of experiment and development to support these future visions lies!

I do not have much time for those who present wild hypotheses, and feel no compunction to generate the proof themselves, placing the onus on their critics to assemble the falsifying evidence. I consider this to be scientific irresponsibility of the highest order, bordering on the unethical. Furthermore, I am also not that enamored by hypotheses, which are not amenable to testing by state-of-the-art technology.

Harold Kroto

In taking a look ahead at the future of organometallic chemistry, it is obvious to think initially of the current drivers of research direction and assume that the directions upon

which we embark today will influence what we discover tomorrow. Although agendas vary across national boundaries, those areas that are most readily highlighted on the basis of societal needs are also those that tend to attract ring-fenced pools of research funding (e.g., energy supply and security; managing and alleviating climate change; feeding the world's growing population; water safety and supply; pharmaceutical development; education; threat detection and alleviation; materials for tomorrow's world). Naturally, it is hoped that such targeted funds will help to secure appropriate basic research and the necessary follow-through to implementation of solutions that might be identified. One can expect that such funding regimes will also spur development in closely allied lines of research.

Against the background of research drivers that stem from readily identified problems and large scale targeted funding it is also necessary to encourage individual ambition, and provide opportunities to first observe, and subsequently follow up, unusual results.

Basic science is often labeled “curiosity-driven”. But all research is fundamentally motivated by curiosity. Different sorts of science are interdependent and equally important. We must not lose sight of the ways in which they reinforce one another.

The Scientific Century Report, The Royal Society

By its very nature, science that has near to market commercial spinoff must be directed by what we already know and driven to achieve a goal that has been clearly enunciated. There is usually little scope within targeted funding regimes to pursue the truly unexpected. In whatever funding models are adopted, and in addition to whatever encouragements are offered to promote work in an identified area, there must always be some room for the curiosity-driven research. Work for which no obvious commercial application can be easily

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attributed often has great value when we recognize that the most amazing discoveries are usually made when looking for something else.<sup>1</sup> We must be ever mindful of the need to support the “what if” and “what next” brand of thinking that has inspired this issue of the journal.

The most exciting phrase to hear in science, the one that heralds new discoveries, is not “Eureka!” (I found it!), but “That’s funny...”

Isaac Asimov

So where might organometallic chemistry be heading in the future, given a global backdrop of more or less obvious problems and as yet unidentified solutions, and the desire to discover the truly new? If one takes a holistic view of the nature of the great challenges that confront our world, a smaller number of cross-cutting research areas and directions can be identified (energy supply, climate stabilization, development of new functional materials, control of reactive intermediates for atom efficient synthesis, etc). Within this article we address the possible outcomes that might arise from the development of highly refined levels of control over electron transfer processes initiated within organometallic complexes and between complexes and surfaces.

## Discussion

**Energy and the Photochemistry of Organometallic Complexes.** Photovoltaics provide a direct, at point of use, method for the conversion of solar energy to electricity and are widely regarded as being key components of a future energy mix. Organometallic complexes hold incredible potential for use as photosensitizers in dye-sensitized solar cells (DSSC), and yet despite the vast efforts expended, few dyes have emerged that can outperform the bis(isocyanato)bis-(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) dye/TiO<sub>2</sub> semiconductor/iodide, triiodide electrolyte based systems. The challenges in arriving at a de novo solution to the dye, semiconductor, and electrolyte combination are considerable. The ideal dye (or suite of dyes) must exhibit broad-spectrum absorption characteristics that not only collect the ultraviolet and visible light energy but also harvest the immense power that reaches the earth in the near-infrared region. The energy of the photogenerated excited state must be well-matched to the conduction band of TiO<sub>2</sub> or other semiconductor of choice, while the redox potentials of the ground state must be compatible with a stable and reliable redox couple within the electrolyte. From a materials chemistry perspective, organometallic precursors that permit the deposition of TiO<sub>2</sub> and other semiconductors with controlled morphology and (nano)crystalline domains merit wider investigation,<sup>2</sup> provided issues of carbon contamination can be avoided. The physical adsorption of the dye to the semiconductor must permit effective electron injection from the photoexcited dye as well as good adhesion and long-term physical device stability. Finally, the kinetics of the various electron transfer reactions must be favorable for charge injection and transfer, rather than permitting direct recombination. Realizing significant advances in DSSC technology will demand not only precise control over absorption profiles

of the organometallic chromophore but also a detailed understanding of the molecule-surface contact chemistry and charge injection processes. While the absorption profile is defined by energy gaps, charge injection and redox cycling rest on the energy of ground and excited states relative to the conduction/valence bands of the semiconductor and the redox potential of the complex relative to the electrolyte redox couple. Such a fine level of control over molecular electronic states will necessitate cooperation between those versed in synthesis, photochemistry, electrochemistry, molecular modeling, electronic structure calculations, and surface chemistry, not to mention the engineering aspects necessary to realize device construction.

A similar checklist of challenges described for the development of optimal photosensitizers in DSSC (i.e., designed absorption profiles, ground- and excited-state energies chosen to meet a specific purpose, controlled interfacial charge injection, and balanced charge transport) also underpins developments in other areas, such as OLED (which on the basis of the prevalence of cyclometalated lumophores are increasingly becoming organometallic, rather than organic, light-emitting diode)-based displays and lighting. Indeed, it is tantalizing to consider the global energy saving that could be achieved from white OLED based domestic lighting.

The global energy mix is complex, and demands for energy in different contexts require an interactive mix of energy solutions. Thus, while photovoltaics might offer a (partial) solution to the electricity demands of a household, and perhaps even provide the energy density necessary to run a car, it is rather more difficult to envision a solar-powered jet airliner. However, if a suitable waste biomass or syngas mixture could be converted to a high-energy-density liquid fuel in an energy-efficient manner, then it may be possible to design alternative aviation fuels (noting the extremely high demands of the aviation industry in this regard and the FAA's commitment to promoting and monitoring change through the Commercial Aviation Alternative Fuels Initiative).<sup>3</sup>

Photoexcited states are remarkable high-energy intermediates, and harnessing these provides an opportunity for achieving chemical reactions without the provision of thermal energy. For example, the development of a solar-powered Fischer–Tropsch catalytic cycle would open vast new opportunities for liquid-fuel sources.<sup>4</sup> Similarly, a photochemical Haber cycle would reduce the energy demands of nitrogen fixation, and while inorganic fertilizers alone cannot solve the impending global food crisis, it may at least buy us time to fully debate the issues surrounding drought/pest/disease resistant GM crops. More widely, solar photocatalysts have potential to completely redefine the way in which we think about small molecule synthesis in solution. Conventional synthetic strategies often rely on the relationship between the Boltzmann distribution of molecular energies at a given temperature and reaction activation energy, and are readily grasped by even the most naive undergraduates (i.e., if a reaction is not proceeding at room temperature, try heating it at reflux...). However, heating reaction vessels costs considerable amounts of energy. The development of less energy intensive forms of processes that are carried out on the vast scale, such as the Haber process, would play a

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huge role in limiting global CO<sub>2</sub> emissions and fossil fuel consumption.

Hydrogen has long been considered as an alternative fuel vector to liquid fuels in some applications, although a myriad of scientific and technological challenges remain to be resolved (e.g., low-energy hydrogen generation, safe and high-density hydrogen storage, optimal fuel-cell design, and long-term component stability). Nevertheless, with the rapid advances in hydrogen fuel cells for automotive applications,<sup>5</sup> the realization of a truly viable contribution from hydrogen to a future energy mix might ultimately rely upon developing the technology for clean H<sub>2</sub> production. The search for a viable hydrogen production strategy is well underway, with the case being made for technologies including electrolysis of water, steam re-forming of CO<sub>2</sub> or methanol, gasification of coal or heavy hydrocarbons, the oxidation of biomass or biohydrogen production from green algae. While conventional industrial production of hydrogen from fossil fuels will probably dominate hydrogen production in the near future, a less energy intensive process of production would seem to hold appeal for use in the long term.

If generation of hydrogen from electrolysis is to be viable, a “clean” source of electricity is necessary. However, while generation of hydrogen from solar-powered electrolysis has the potential to provide a long-term solution, the material costs of crystalline photovoltaics are too high to meet cost targets for hydrogen (2–4 c/kWh). DSCCs offer an alternative as an electricity source for hydrolysis, provided sufficient potentials can be achieved, but photosynthetic microbial systems that produce hydrogen from water may be a key here, not least of all being the use of sunlight as the primary energy source to generate hydrogen directly. The integration of biological systems into a hydrogen production cycle will require more integrated approaches from molecular chemistry (and here the organometallic chemist has a pivotal role in working with the hydrogenase enzyme active site) and genomic and bioengineering research.

In the biological systems, protein structures and active sites in enzymes have evolved to cope with the remarkable challenges of promoting the conceptually simple electrochemical half-reactions  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  and  $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ , which together give the photochemical splitting of water. In order to achieve viable catalytic turnover rates, nature has evolved a complex protein host environment, in which closely controlled geometries, binding sites, pH and electron transfer pathways, and kinetics provide extraordinarily facile pathways for reactions.

At the present time, artificial small-molecule structures cannot hope to mimic directly the action of the natural system: engineering the active site itself is sufficiently challenging. For example, in the “iron-only” hydrogenase,<sup>6,7</sup> the bimetallic iron active site is supported by a combination of carbonyl (CO) and cyanide (CN<sup>−</sup>) ligands, together with a cluster-based redox shuttle. This incredibly effective system might be thought of as rather unusual for a biological system, but an ideal playground for the organometallic chemist. However, developing mimics of the protein environment (for example, in the case of the iron-only hydrogenase, the H-bonding interactions between cyanide ligands and the

protein support that are thought responsible for maintaining the relative metal geometries in the native enzyme) is a challenge likely to remain beyond us for a considerable period of time. Indeed, the complexities of electron-transfer reactions in biological systems and those coupled with ion and/or proton transfer still remain a topic of great debate and profound importance to the design of biomimetic or bioinspired molecular machines.<sup>8,9</sup> In the future, a combination of chemistry and biology may lead to the designed synthesis of such structures by employing proteins as ligands. Nevertheless, bioinspired approaches, in which inspiration for molecular design is drawn from Nature’s blueprint, are far more tractable. For example, the key structural elements of the [2Fe2S] enzyme active site from iron-only hydrogenases can be engineered in bimetallic models, and efforts to link a cluster model of the [4Fe4S] redox shuttle to the bimetallic reaction center are underway.<sup>10</sup>

Photogeneration of hydrogen using metal catalysts has been a hot topic for some time now,<sup>11</sup> and as described above, the organometallic chemistry of the Fe<sub>2</sub>(μ-dithiolate) systems, driven by the relevance of such studies to the iron-only hydrogenase active site, is exceptionally well developed. However, studies of photochemical activation/reduction of the bimetallic iron models are more limited.<sup>12–16</sup> While active toward photochemical reduction of protons (thereby demonstrating proof of principle), few of the photoactive hybrid systems described to date have attempted to use bimetallic iron systems more complex than the simple Fe<sub>2</sub>(μ-dithiolate)(CO)<sub>6</sub> cores, and turnover numbers are generally low. A collaborative approach in which coupled electrochemical–photochemical reaction chemistry and organometallic chemistry are linked with insight from biology and implemented through materials science and engineering will be necessary to tackle the challenges associated with designing a *photocatalyst* capable of operating within the solar spectrum that mediates the proton-coupled multielectron-transfer reactions associated with water splitting. In the ultimate scenario, the photochemically driven proton-reduction half-cell would be coupled with a photocell driving the oxidation of water ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ) to achieve the complete photochemical splitting of water to O<sub>2</sub> and H<sub>2</sub> under solar irradiation. Recent advances in the design of bioinspired water-oxidation photocatalysts, based on manganese oxo clusters,<sup>17–20</sup> suggest that while such activity is

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difficult, it is most certainly feasible. Given the essential role polymetallic species play in nature's electron transfer cascades and reaction sites, perhaps a renaissance of cluster chemistry is due, driven not by a cluster-surface analogy but by a cluster-enzyme analogy. In a cluster-enzyme analogy inspired research environment, "traditional" pyrolysis reactions of clusters would be replaced by studies of redox and (photoinduced) electron transfer processes, the purpose of which would not be to find new cluster rearrangements but rather to identify metal frameworks able to act as structurally robust redox shuttles and reaction sites.

**Organometallic Complexes in Molecular Electronics and the Case for Ground-State Electronic Processes.** While the future for the use of organometallic photoexcited states seems bright, ground-state electron transfer processes in organometallic complexes also offer many exciting opportunities for the future. Undergraduates are taught that metal complexes are distinguished from organic compounds by the presence of valence electrons in *d* orbitals and how the population and depopulation of these high-lying electron sinks lead to variable spectroscopic and magnetic properties. Control and manipulation of these states has long been a challenge, as efforts to design high-performance single-molecule magnets will attest. The control and manipulation of metal redox and spin states at the molecular level also promise a great deal in terms of the future development of molecular electronics.

Moore's Law, the observation that the number of components that can be placed on a silicon chip approximately doubles every 2 years, with commensurate increases in the processing and data storage capacities of devices and decreases in the unit cost of components, has driven decades of technological achievement and new materials science.<sup>21</sup> Devices with < 45 nm feature sizes are now in production, and, if Moore's Law is to continue to operate *in the longer term*, further reductions in feature size will be required. Therefore, industry is now looking at the materials challenges required to be addressed for the next few years if 22 nm feature sizes, and even smaller, are to be achieved in the future. Two consequences flow from the desire to maintain technological pace with the demands of Moore's Law. The first is that, in the medium-long term, feature sizes will approach molecular dimensions. The second is a more practical and immediate consequence; new materials must now be integrated into silicon-based devices. For example, even in the present generation of 45 nm chips, silicon dioxide is no longer used as the gate insulator in the transistors, because at the feature sizes required, a SiO<sub>2</sub> gate needs to be so thin that it would leak too much current when the transistor is in the "off" state. This problem was recognized long before the exact materials solution was conceived, even though the nature of the solution (a high- $\kappa$  alternative insulator) was apparent.<sup>22,23</sup> After a relatively brief but intense search, hafnium oxide was identified as a viable alternate insulator material. The technical challenges inherent in depositing HfO<sub>2</sub>, a highly refractory and expensive material,

instead of simply oxidizing silicon, were considerable.<sup>24–27</sup> However, driven by the industrial and consumer demands to meet Moore's Law, the materials science and deposition chemistry challenges were met, and HfO<sub>2</sub>-containing integrated circuits are now being sold worldwide.<sup>28</sup> The point to be made here is that the introduction of new materials into the production stream of advanced electronic devices is an established part of the device evolution. Another evolutionary requirement for the future will be the replacement of polysilicon contacts with metal; polysilicon is simply too resistive at the contact sizes required for < 45 nm devices and would generate too much heat, but there will again be formidable challenges in laying down metal contacts at these feature sizes,<sup>29</sup> and new precursors for controlled metal deposition and etch systems will be required. It is clear that traditional silicon-based technology is already undergoing major changes, and while molecular electronics is commonly perceived to be very difficult to implement, the continued development of "traditional" silicon technology also faces profound challenges.

The term "molecular electronics" is generally applied to structures designed to involve a single molecule, or a single layer of molecules, oriented between two contacts (which may be metals or semiconductors), with the critical dimension between the contacts therefore lying in the nanometer size range. Circuit components at the molecular level could exploit the small size of molecules and their enormous potential variation in structure and properties, controlled using the tools of synthetic chemistry, to increase device density and to incorporate new functionality into existing or new microelectronic architectures. In order to utilize molecules in electronic devices, it is clear that a major paradigm shift will be needed from current silicon-based technology, and it is therefore likely that, as recently with "plastic electronics" (i.e., electronics using the bulk properties of conjugated polymers), new technologies and opportunities for both research and application will evolve.

Some 35 years after the Aviram–Ratner molecular rectifier was proposed, the International Technology Roadmap for Semiconductors (ITRS) has set a timeline that will move the field of molecular electronics from the pure research phase (2009–2018), through development (2019–2021) and into production (2022 onward).<sup>30</sup> Molecular systems offer considerable theoretical advantages on cost, scalability, component density, and power consumption criteria when weighed against solid-state materials. The transition from purely solid-state electronics to hybrid molecular/solid-state technology will require many technological challenges to be met and overcome, including (1) production of molecular materials with appropriate dimensions to interface with fabricated solid-state device features, (2) development of methods for tethering active molecular components to a solid surface in such a way as to provide robust and electronically useful junctions, (3) assembly of molecule/solid-state devices, (4) measurement, interpretation, and application of the electronic characteristics of the hybrid molecular/solid-state device structure.

To date, significant effort has been expended toward meeting one or other of these goals principally through the use of organic molecules and gold–thiol (Au–SR) self-assembled

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monolayers (SAMs). Organometallic complexes, which combine organic and inorganic (metal centers and clusters) components, represent in many ways the ultimate in molecular species for use in hybrid molecular/solid-state constructions, with exquisite atomic-level control of structure afforded by synthetic chemistry coupled with the electronic and magnetic diversity offered by elements chosen from across the whole periodic table. Therefore, organometallic complexes represent an attractive family of molecular materials that have received far less attention for molecular electronics applications than other materials (e.g., carbon nanotubes, graphitic materials and graphene, SAMs of organic thiols on gold, DNA). To date, the significant majority of molecular systems investigated for molecular electronics purposes have been purely organic in composition. A vast array of organic molecular systems have been explored either as passive, wirelike components in their own right or as tools through which to investigate fundamental issues (connection to electrodes, through-molecule conduction vs. formation of metallic filaments, conduction vs. length, etc.), including simple  $\alpha,\omega$ -functionalized alkanes and, commonly, oligomeric phenylene(ethynylene) systems. Organic structures of remarkable length have been prepared,<sup>31,32</sup> providing the capacity to manipulate molecular systems within the demanding constraints imposed by electronic test-bed devices. More highly functional (i.e., redox-active) structures have also been considered both experimentally<sup>33–37</sup> and theoretically.<sup>38</sup> The role that redox and magnetic processes play in manipulating the  $I-V$  response of these devices containing redox-active molecular components is a source of considerable optimism from the point of view of engineering higher order electronic function and for spintronic applications. Indeed, the opportunity to control access to particular molecular charge states via a gate electrode and/or an external magnetic field opens an immense range of opportunities for the construction of highly functional hybrid molecular/solid-state devices.<sup>39,40</sup> However, only in the past few years has there been a concerted effort to

examine the molecular electronic potential of metal-containing molecular materials.<sup>41–50</sup>

Organometallic complexes possess properties that make them particularly attractive candidates for emerging research materials for electronics. These include the following, controllable through synthetic chemistry:

- versatility of structure, length, and binding groups, including control of the ligands, of stereochemical and geometric structure at the metal center(s), and of spin state at the metal center, with possible implications for spintronics applications;
- control of redox chemistry and multiple redox states enabling development of device functionality and enabling gated control of electronic function;
- control of charge transport mechanisms from shorter range superexchange to longer range hopping;
- potential for modular construction.

In contrast to the wide variety of organic compounds that have been assembled within molecular electronics test beds, studies of metal-containing molecules are far more limited, despite the undoubted potential of such systems. The role of metal complexes in hybrid devices was recently underlined by a number of important works describing Kondo effects in hybrid devices.<sup>40,51,52</sup> Together, these publications demonstrate that redox and magnetic effects within the metal complex are important and potentially immensely useful phenomena, with opportunities for further functional tuning arising from the nature of the contacts between the complex and the electrode surfaces.<sup>53</sup> These works have spurred a wave of interest in hybrid devices in the past few years. Progress has been made in the attachment of organometallic complexes to surfaces, which has included covalent attachment,<sup>54</sup> assembly into SAMs,<sup>55</sup> contacting complexes with gold nanoparticles,<sup>56</sup> and immobilization of metal-containing compounds between nanoscale electrode gaps.<sup>57</sup> More modular approaches to the construction of the electronically active complexes by synthesis on the surface have also appeared recently, and the activity is reflected in the recent reviews of the area.<sup>58–60</sup> Top contacting of these

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“on surface”-synthesized complexes has been achieved by the introduction of metallic nanoparticles<sup>61</sup> or a mercury drop electrode.<sup>62</sup> Of considerable importance is the demonstration of the contact-limiting resistance of the latter structures.

It is therefore apparent that, at the present time, both preformed and “on surface”-synthesized metal complexes offer viable routes to hybrid device structures. The readily accessed and tunable redox properties of the organometallic compounds coupled with the ability to exploit organic structures within and pendant to ligands around the metal center permits considerable scope for the development of highly functionalized molecular-based devices (e.g., gated charge transfer) with a level of control and expediency beyond that commonly achieved with “purely” organic molecules. However, issues surrounding the molecule-surface contact and the methods of reliably fabricating a top contact remain to be systematically explored, and the role of redox and spin states within complexes on the electronic characteristics of hybrid devices, especially in back-gated architectures, demands further investigation.

Computational chemistry will play an essential role in the design of molecules that fulfill functional roles in these areas. The immense contributions of *ab initio* and density functional based calculations to the interpretation of spectroscopic data, reaction profiles, and physical structure cannot be underestimated. At some point in the future, computational chemistry will provide a step-change in the way molecules are designed and materials for investigation are selected, but only when computational protocols are developed that permit the accurate modeling or prediction of

charge-transfer energies and molecule-surface interactions. Basis sets that accurately deal with the heavier elements, density functionals that overcome the electron-hole correlation problem associated with modeling charge-transfer processes, and accurate solvation models are all desperately required to improve the accuracy of computational predictions. Close work between experimentalists, computational chemists, and theorists will be required before such a goal can be achieved.

## Conclusion

In summary, the manipulation of electrons around an organometallic framework, be it in response to an incident photon or an externally applied electric field, hold vast promise for future applications. The realization of organometallic-based systems will necessitate close collaboration between the practitioners of diverse disciplines from synthesis through photochemistry and redox chemistry, computation and modeling, biology, engineering, and physics. Nature uses metal centers and clusters to store, promote, and shuttle electrons to do useful work: it seems likely that we should follow her lead.

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