1.2
Dendrimers

1.2.1
History and terminology

The term "*dendrimer*" comes from the Greek and is a combination of the words dendron, meaning "tree", and meros, meaning "part", and was introduced by *D. A. Tomalia* in 1985.[59] The 1978 publication of *F. Vögtle et al.* laid the foundation of the preparation of dendritic molecules,[60] which have attracted considerable attention in the last decades in the field of supramolecular chemistry, and also in theoretical, physical, polymer, and inorganic chemistry due to their material properties as well as in biotechnology.[61] Such branched or even hyperbranched molecules called arboroles[62], cascade molecules,[60] dendritic molecules, or starburst-dendrimers[59] are constructed from identical monomeric building blocks carrying branching sites which are located in a spherical way around a core. The shells of monomers are called generations (**Figure 1.3**). On the periphery, dendrimers can carry numerous functional groups that can finally lead to a surface congestion due to their steric interactions (dense-packed stage or "starburst").[63, 64]

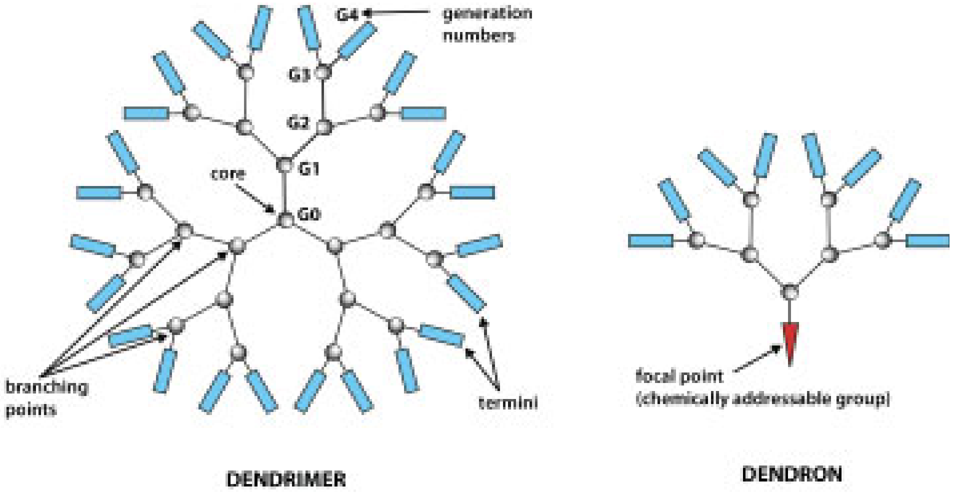


Figure 1.3 Terminology used for dendrimers. Figure based on an image which was published under public domain licensing.[65]

1.2.2
Construction of dendrimers

The synthesis of uniform dendritic molecules can proceed in two iterative ways. Firstly, the *divergent-iterative* pathway (**Figure 1.4**), which was used in the early work in 1978, starts from an initial core with two or more functional groups. These are converted using monomers with protected reactive sites. The removal of the protecting groups and the repeated reaction with monomer units leads to an exponential increase of functional groups on the surface of the spherical molecule.[64]

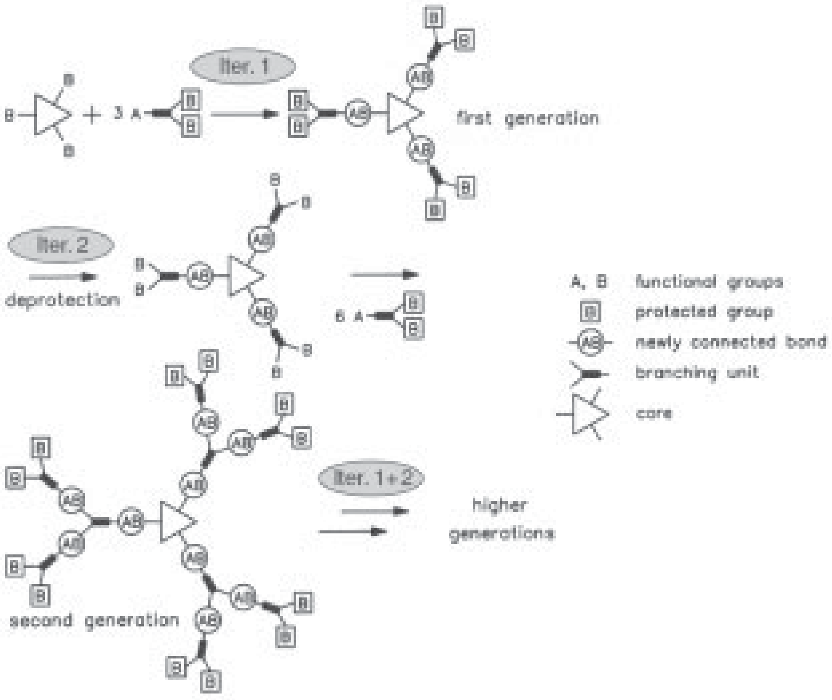
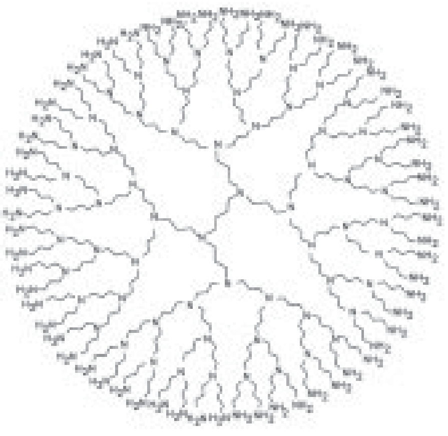


Figure 1.4 Divergent-iterative synthetic pathway for the preparation of dendrimers. Figure taken from literature.[64]

With this method, new dendrimers were prepared in the following years by *R. G. Denkewalter et al.*,[66] *D. A. Tomalia et al.*,[67] *G. R. Newkome et al.*,[68] and by *F. Vögtle et al.*[69] Following a reaction pathway similar to the one used in 1978, *E. W. Meijer et al.* successfully synthesised a polynitrile dendrimer up to the fifth generation on a large scale (**Scheme 1.1**).[70]



Scheme 1.1 Polyamine dendrimer of the fifth generation obtained on a kilogram scale.

A potential source of structural imperfection is the rapid increase of reactive groups as growth is pursued. Their incomplete conversion leads to defects inside the molecule.[71] In the second major iterative pathway, called *convergent-iterative* synthesis, these problems are avoided by directing the dendritic growth from the surface inwards to a focal point. In a final step, several dendrons are connected with a multifunctional core to yield the desired dendrimer (**Figure 1.5**).[64]

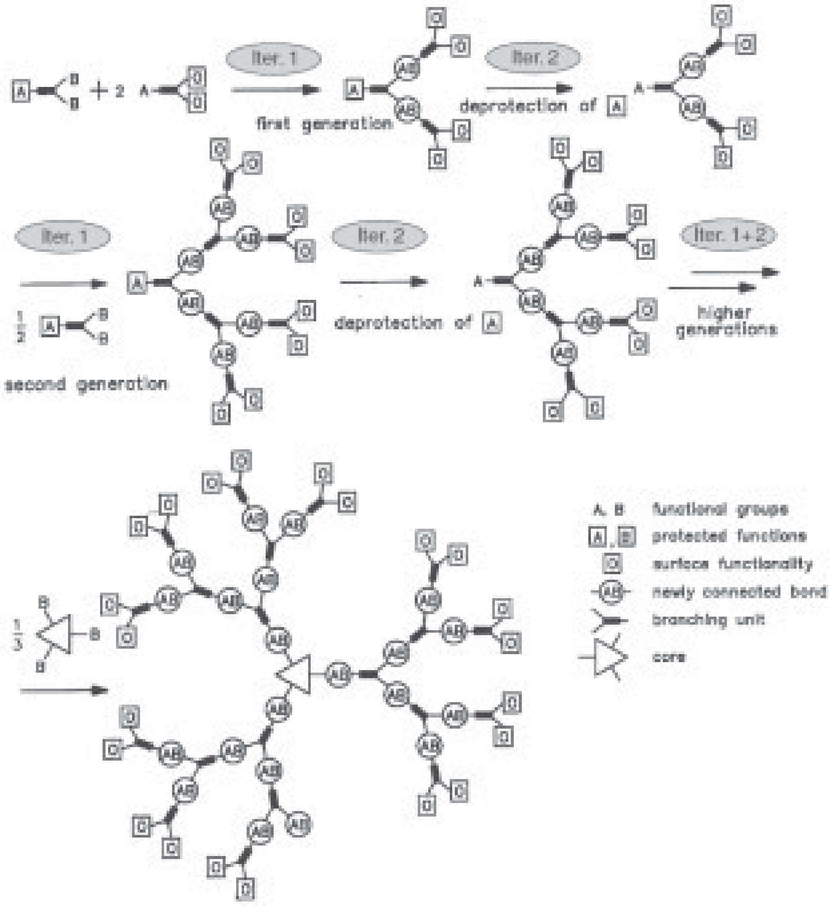


Figure 1.5 Convergent-iterative synthesis of dendritic molecules. Figure taken from literature.[64]

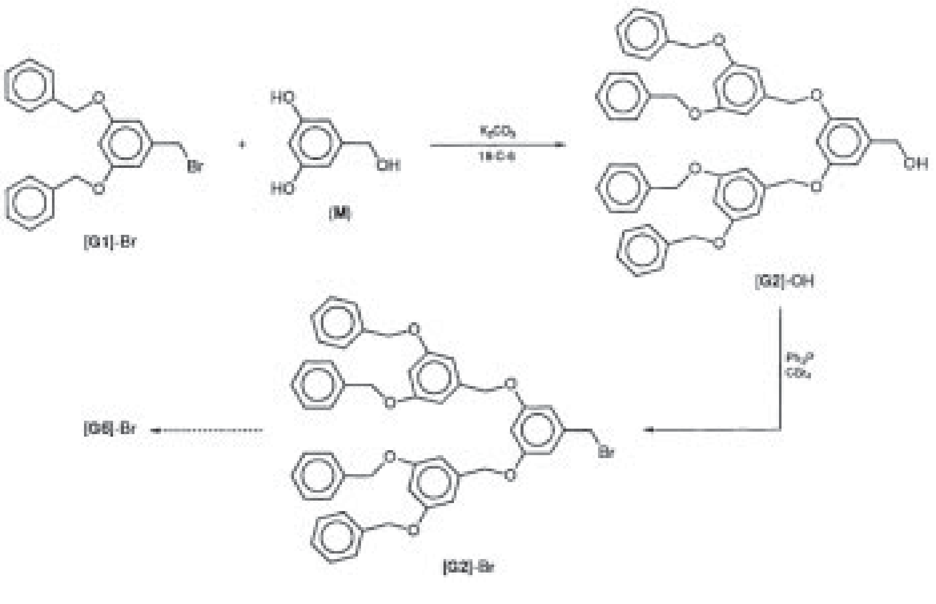
A large family of new dendrimers has been synthesised following this divergent method. *C. J. Hawker* and *J. M. J. Fréchet* developed polyaryl(-benzyl)ether dendrimers (see **Section 1.2.3**),[71] *T. M. Miller* and *T. X. Neenan*,[72] and also *J. S. Moore* and *Z. F. Xu*[73] prepared hydrocarbon dendrimers. The latter have reported the largest monodispersed organic hydrocarbon dendrimer with a molecular mass of 18 kDa and a diameter of 12.5 nm.[74]

Comparison of these two methods shows that generally dendrimers prepared by the divergent approach are more polydispersed than those prepared by the convergent route.[75] In the divergent methodology, a significant feature is the rapid increase in the number of reactive groups at the periphery of the growing macromolecule.[21] Potential problems which may arise as growth is pursued include incomplete reaction of these terminal groups, especially at higher generations when large numbers of reactions have to occur on a sterically hindered dendrimer surface. This would lead to imperfections in the next generation, or the use of large excess of reagents that are required to force reactions to completion. This, in turn, presents difficulties in purification.[21]

The convergent method, on the other hand, is usually limited to dendrimers of lower generations due to the steric hindrance at the focal points of large dendrons. Stoichiometric reactions are therefore crucial for every step.

1.2.3
Fréchet-type dendrimers

C. J. Hawker and *J. M. J. Fréchet* described the first example of dendrimers constructed by the convergent approach (see previous section).[71, 76] The so-called Fréchet-type dendrimers consist of polyether fragments which are prepared by starting from what will become the periphery of the molecule.[77] The synthesis then progresses inward. In their very first example, the first step is a condensation of two equivalents of benzyl bromide with two phenolic groups of the monomer, *i.e.* 3,5-dihydroxybenzyl alcohol (**Scheme 1.2**). After transformation of the benzylic alcohol functionality into the corresponding leaving group (*e.g.* bromide or mesylate), the procedure is repeated with stepwise addition of the monomer followed again by activation of the benzylic site.[21] As discussed in the previous section, this method of building up dendrimers has been established as the ideal system to construct dendrimers when lower generations are needed. In this thesis, Fréchet-type dendrons were used to study their 2D self-assembled monolayers on graphite.



Scheme 1.2 Synthesis of a Fréchet-dendrimer. Figure taken from literature.[71]

1.3
Coordination chemistry

1.3.1
History and concepts

It is difficult to trace back the history in the area of *coordination chemistry*, as there is, in fact, no defined beginning.[78] The synthesis of certain compounds, of which the crucial ingredient is a coordination compound, has been performed, and also documented, in ancient times already. The first scientific evidence for the formation of a coordination compound is the preparation and characterisation of $[Cu(NH_3)_4]^{2+}$ by *A. Libavious*, a physician and alchemist, in 1597.[79] Although he did not isolate the product, *Libavious* observed a blue colouration when a solution of $Ca(OH)_2$ on a bronze surface was treated with NH_4Cl.[80]

The beginning of *coordination chemistry*, as we know it today, is often referred to *A. Werner*. He introduced a theory[8] which allows us to understand the difference between coordinated and ionic chloride in the cobalt ammine chlorides and to explain many of the previously inexplicable isomers.[81]

Coordination compounds, also known as metal complexes, include all metal compounds, aside from metal vapours, plasmas, and alloys.[81] The study of "*coordination chemistry*" is the study of the inorganic chemistry of all alkali and alkaline earth metals, transition metals, lanthanides, actinides, and metalloids. Thus, coordination chemistry is the chemistry of the majority of the periodic table. Metals and metal ions only exist, in the condensed phases at least, surrounded by ligands.

Mononuclear transition metal complexes are prepared by reacting a metal ion (M) with a number of free ligands (L) (**Scheme 1.3**).

$$M \quad + \quad nL \longrightarrow [ML_n]$$

Scheme 1.3 Reaction of a metal ion (M) with a number of free ligands (L).

Whereas the effect of the ligands upon a metal ion is relatively well understood, and moderately easily quantified, the converse effect is not so.[82] In particular, the change from lone pair to bonding pair, consequent upon the formation of the coordinate bond (**Figure 1.6**), has effects upon the other groups which might be bonded to the ligand donor atom(s).

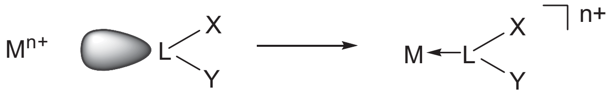


Figure 1.6 Schematic representation of the formation of a coordination compound, emphasising the conversion of the ligand lone pair to a bond pair.

There are several changes which result from coordination of a ligand to a metal.[82]

(a) *Conformation changes* can occur in the equilibrium conformation of the coordinated ligand with respect to the equilibrium conformation of the free ligand. A lone pair from the ligand bonds to a metal. The bonding changes the non-binding interactions in the molecules and we can see changes in bond lengths, angles, and molecular geometry.

If a polydentate ligand binds to a single metal, the resultant complex is a chelate (Greek "chelos", claw). Chelate complexes are more stable, with respect to ligand displacement, than a compound with equivalent monodentate ligands. The coordination follows a pathway in which metal-ligand formation is sequential.

An example of this is the conformational changes of 2,2'-bipyridine (see **Section 1.3.2**) when coordinated to a metal. The conformation is altered from *transoid* to *cisoid*, as shown in **Figure 1.7**. These changes can be monitored by the downfield shifting of the signal for H^3 comparing the ^1H NMR spectrum of the free ligand and complex. This is a consequence of the steric repulsion between the H^3 atoms in the *cisoid* conformation of the complex.

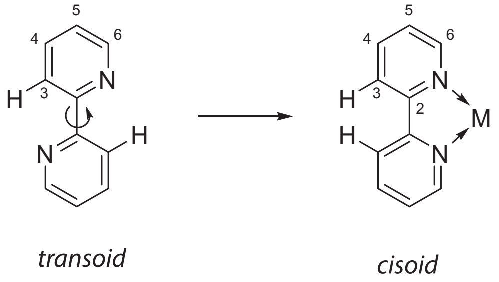


Figure 1.7 Conformational change upon coordination of 2,2'-bipyridine.

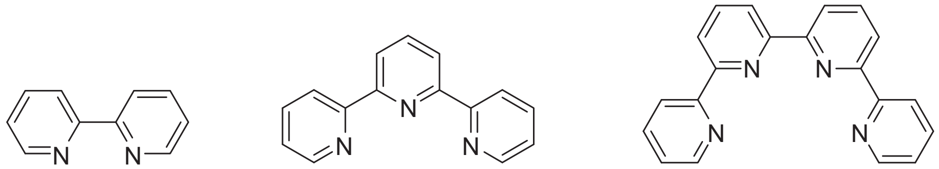
(b) *Polarisation changes* may occur upon complexation. If the metal ion to which a ligand is coordinated is in a non-zero oxidation state, it will exert an electrostatic effect upon the bonding electrons of the ligand. This will result in the induction of a net permanent dipole in the ligand, with any associated chemical and physical effects. Even zero-oxidation state metal centres may induce a polarisation in the ligand through electronegativity or induced dipole-dipole effects.

(c) *π-Bonding changes* will take place by the introduction of π-bonding interactions between the metal and the ligand. The coordination process results in a metal-to-ligand or ligand-to-metal transfer of electron density, depending on the nature of the metal centre, its oxidation state, and on the nature of the ligands. This opposes the polarisation effects of the metal ion in many cases.

The understanding of all these effects has led to a better understanding of the chemistry of organometallic and bio-inorganic systems. The explanation gives a versatile description of an enormous range of ligand reactions.

1.3.2
Oligopyridines

Oligopyridines are molecules made (formally) by bonding pyridine subunits together through C–C bonds. The most commons ones are represented in **Scheme 1.4**.



2,2'-bipyridine (bpy) 2,2':6',2''-terpyridine (tpy) 2,2':6',2'':6'',2'''-quaterpyridine (qtpy)

Scheme 1.4 The most common oligopyridines.

The names come from the Greek prefix for the total number of pyridine rings combined with the word "pyridine". The position is specified with the nitrogen at the first position and subsequent rings are denoted with primes.

2,2'-Bipyridine, is, undoubtedly, the most commonly used representative ligand in the class of oligopyridines, and its derivatives are renowned for their ability to form coordination compounds with metal ions of almost all groups in the periodic table.[4] It is a molecular building block *par excellence* for a wide variety of types of molecular and ionic aggregates ("supramolecules", see **Section 1.1**). Pure 2,2'-bipyridine was synthesised and analysed by *F. Blau* in 1889, when he obtained it by distillation of copper picolinate.[83] One year before, in 1888, *Blau* synthesised the first complexes of Fe(II) salts with 2,2'-bipyridine and isolated a series of salts with the composition $[Fe(bpy)_3][X]_2$.[84, 85] As metal complexes usually are readily obtained upon addition of the free ligand bpy to the metal ion, and as the complexes normally exhibit a very high stability, 2,2'-bipyridine complexes are used in analytical chemistry for the determination of metals, especially Fe(II).[86] 2,2'-Bipyridines can also influence biological systems.[87, 88] Their activity is usually a consequence of their ability to complex those metals which are jointly responsible for the enzymatic activity in a living organism. Moreover, they are able to stimulate the activity of some enzymes, probably by removing the metal which inhibits them.[87]

1.3.3
Iridium and its complexes

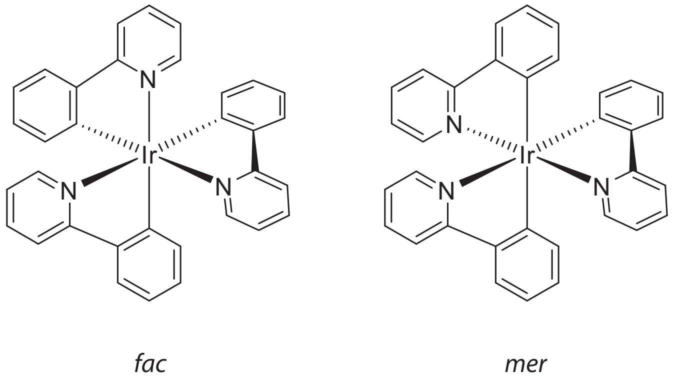
The element iridium is a very hard, brittle, silvery-white transition metal of the platinum family. Iridium is the second densest element (after osmium by about 0.1 %) and is the most corrosion-resistant metal, even at temperatures as high as 2000 °C.[89] Iridium (Greek "*iridios*", meaning rainbow-like colours, named by the manifold colours of its compounds) was discovered in 1803 by

S. Tennant among insoluble impurities in natural platinum from South America.[90] Iridium is one of the least abundant elements in the Earth's crust. With an average mass fraction of 0.001 ppm in crustal rock, it is four times less abundant than gold, ten times less abundant than platinum, and eighty times less abundant than silver and mercury.[91] An alloy of 90 % platinum and 10 % iridium was used in 1889 to construct the international prototype meter and kilogram mass, kept by the "International Bureau of Weights and Measures" near Paris.[92] Interestingly, iridium has been linked with the extinction of the dinosaurs and many other species 65 million years ago. The unusually high abundance of iridium in the clays of the K–T geologic boundary (Cretaceous and Tertiary periods) was a crucial clue that led to the theory that the extinction was caused by the impact of a massive extraterrestrial object with the Earth, the so-called *Alvarez* hypothesis.[93]

Iridium forms compounds in the oxidation states of −3 and all in the range from −1 to +6, the most common oxidation states are +3 and +4.[91] Trihalides of iridium, *i.e.* IrX_3, are known for all of the halogens. $IrCl_3·3H_2O$ was used for the preparation of the Ir(III) complexes presented in **Chapter 7**. In the solid state of the trihalides, in fact for all halides of IrX_n (n = 1, 3, 4, 5, 6), each metal centre is in an octahedral environment.[90]

Iridium(III) complexes, exhibiting a [Xe] d^6 electron configuration, generally adopt the coordination number six. Normally, they possess diamagnetic properties due to the low-spin $t_{2g}^{\ 6}\ e_g^{\ 0}$ configuration in the complex, as the iridium(III) cation (as a third row transition metal) has a large contribution to the ligand field stabilisation energy,[90] with a *g*-factor of 32'000 cm^{-1}.[94] The colour of the complexes, often in the range between yellow and red, is due to two electronic transitions from $t_{2g}^{\ 6}\ e_g^{\ 0}$ to $t_{2g}^{\ 5}\ e_g^{\ 1}$ (*i.e.* $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively).[90] Charge transfer bands, on the other hand, may lead to other colours also. Like the Co(III) analogues, Ir(III) complexes possess a *kinetically* high stability due to the highly symmetric electronic configuration. The *thermodynamically* stability ranges from "hard" (*e.g.* F^-, OH^-, NH_3; lower stability) to "soft" (*e.g.* I^-, RS^-, PR_3, CO; higher stability) ligands.[90]

A rather unique feature of the Ir(III) chemistry is the ability to establish bonds to carbon atoms to form extraordinarily (air- and water-) stable complexes. Chelate complexes with, for instance, 2-phenylpyridine (Hppy), such as the homoleptic $[Ir(ppy)_3]$ (**Scheme 1.5**), often described as *cyclometallated* or *orthometallated* compounds,[95, 96] are well known and have a broad application in solid state lighting (see **Section 1.5**).



Scheme 1.5 The two stereoisomers of homoleptic tris(2-phenylpyridine)iridium(III), the *facial* and the *meridional* isomer.

Concerning electronic features of heteroleptic Ir(III) complexes as prepared in **Chapter 7**, calculations of the cations show that both the HOMO and the LUMO are primarily ligand-centred. Whereas the HOMO is mainly found on the phenyl rings of the *C*,*N*-ligands, the LUMO is strictly localised on the *N*,*N*′-ligand (**Figure 1.8**). This is important for colour optimisation regarding the complex's luminescence properties.

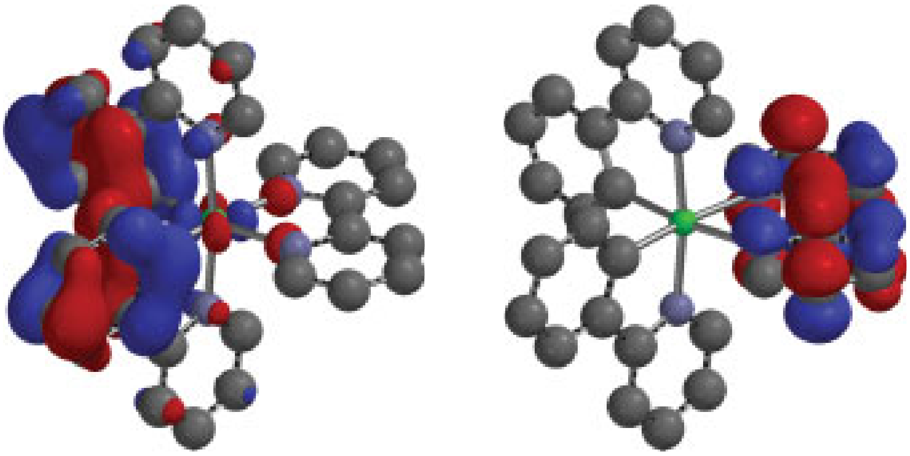


Figure 1.8 Semi-empirical calculations at the PM3 level of the HOMO (left) and LUMO (right) of the solid state structure of the cation in complex **49**.

1.4
Scanning tunnelling microscopy

1.4.1
History

In March 1981, a new type of microscope made its debut.[97] Unlike traditional (optical) microscopes, however, the scanning tunnelling microscope (STM) did not use lenses. Instead, a sharp tip was moved close enough to a conductive surface for the electron wavefunctions of the atoms in the tip to overlap with the wavefunctions of the surface atoms (see also **Section 1.4.2**). The initial results were written up in a manuscript which was submitted to a leading physics journal in June 1981. However, the paper was declined by the editors based on the report of one of the referees who said that the experiment would not give any new insight. Eventually, the results were published in another leading journal, *Applied Physics Letters*, in January 1982.[98] These experiments were conducted in Switzerland at the IBM research centre in Rüschlikon by *G. Binnig* and *H. Rohrer* who awarded the Nobel prize for physics only four years later, in 1986. In terms of science, the real breakthrough for the STM came in 1983 with the experimental observation of one of the most intriguing phenomena in surface science at that time, *i.e.* atom-by-atom imaging of the 7 × 7 surface reconstruction in Si(111).[99] For the first time it was possible to visualise individual atoms on surfaces in a 3D representation.[97]