From STM to LEECs: Syntheses and Applications of Multifunctional Bipyridine Ligands and their Iridium(III) Complexes

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From STM to LEECs: Syntheses and Applications of Multifunctional Bipyridine Ligands and their Iridium(III) Complexes

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I want to express my deepest thanks to the creator of this world.

And God said: “Let there be light”;
And there was light.
And God saw that the light was good.

Genesis 1, 3–4

Contents

Abbreviations

General

2D	two-dimensional
3D	three-dimensional
HOMO	highest occupied molecular orbital
LC	ligand centred
LUMO	lowest unoccupied molecular orbital
MC	metal centred
MLCT	metal-to-ligand charge transfer
MO	molecular orbital
S_0	ground state

Chemical

Aliquat 336	NR_4Cl; R = mixture of $-C_8H_{17}$ and $-C_{10}H_{21}$
aq.	aqueous
Ar	aryl / aromate
bpy	2,2'-bipyridine
Bu	butyl
de	diastereomeric excess
DEAD	diethyl azodicarboxylate
DMF	N,N-dimethylformide
dpbpy	6,6'-diphenyl-2,2'-bipyridine (**32**)
ee	enantiomeric excess
fac	facial
Hbzq	7,8-benzoquinoline
Hdfppy	2-(2,4-difluorophenyl)pyridine
Hdmppz	3,5-dimethyl-1-phenylpyrazole
Hpiq	1-phenylisoquinoline
Hppy	2-phenylpyridine
Hppz	1-phenylpyrazole
L	ligand
M	metal
mer	meridional
n	unspecified number
n-alkyl	normal alkyl, *i.e.* unbranched alkyl
pbpy	6-phenyl-2,2'-bipyridine (**31**)
PCC	pyridinium chlorochromate
PEG-300	polyethylene glycol (average molecular weight of 300 g mol^{-1})

Ph	phenyl
Py	pyridine
phen	1,10-phenanthroline
ppbpy	4,6-diphenyl-2,2'-bipyridine
$(HO)_2$ppbpy	4-(3,5-dihydroxyphenyl)-6-phenyl-2,2'-bipyridine (**37**)
$(H_3CO)_2$ppbpy	4-(3,5-dimethoxyphenyl)-6-phenyl-2,2'-bipyridine (**35**)
$(H_{21}C_{10}O)_2$ppbpy	4-(3,5-bis(decyloxy)phenyl)-6-phenyl-2,2'-bipyridine (**38**)
$(G1–O)_2$ppbpy	4-(3,5-bis(3,5-bis(dodecyloxy)benzyloxy)phenyl)-6-phenyl-2,2'-bipyridine (**39**)
$(G2–O)_2$ppbpy	4-(3,5-bis(3,5-bis(3,5-bis(dodecyloxy)benzyloxy)benzyloxy)phenyl)-6-phenyl-2,2'-bipyridine (**40**)
pphen	2-phenyl-1,10-phenanthroline (**30**)
qtpy	2,2':6',2'':6'',2'''-quaterpyridine
R	(organic) rest
r.t.	room temperature
sat.	saturated
(+)-TADDOL	(4*S*,5*S*)-2,2-dimethyl-α,α,α',α'-tetraphenyldioxolane-4,5-dimethanol
(–)-TADDOL	(4*R*,5*R*)-2,2-dimethyl-α,α,α',α'-tetraphenyldioxolane-4,5-dimethanol
THF	tetrahydrofuran
tpy	2,2':6',2''-terpyridine

Chemical analysis

a.u.	arbitrary units
br	broad (NMR, IR)
calcd.	calculated
COSY	correlated spectroscopy (NMR)
CV	cyclic voltammetry
d	doublet (NMR)
δ	chemical shift (NMR)
DEPT	distortionless enhancement by polarisation transfer
ε	extinction coefficient
EI	electron impact
ESI	electrospray ionisation
FAB	fast-atom bombardment
Fc	Ferrocene
HMBC	heteronuclear multiple bond correlation (NMR)
HMQC	heteronuclear multiple quantum correlation (NMR)
HPLC	high performance liquid chromatography
IR	infrared spectroscopy
J	coupling constant (NMR)
λ	wavelength

λ_{em}	emission wavelength
λ_{ex}	excitation wavelength
m	multiplet (NMR); medium strong (IR); mass (MS)
MALDI	matrix assisted laser desorption ionisation
mp	melting point
MS	mass spectrometry
$\tilde{\nu}$	wavenumber (IR)
NMR	nuclear magnetic resonance spectroscopy
NOESY	nuclear overhauser effect (NMR)
ppm	parts per million (NMR)
q	quartet (NMR)
R_f	retention factor (TLC)
s	singlet (NMR); strong (IR)
t	triplet (NMR)
TLC	thin layer chromatography
TMS	tetramethylsilane
TOF	time of flight
UV-Vis	ultra-violet visible spectroscopy
w	weak (IR)
z	charge (MS)

Scanning probe microscopy

AFM	atomic force microscopy / microscope
HOPG	highly oriented pyrolytic graphite
SAM	self-assembled monolayer
SPM	scanning probe microscopy / microscope
STM	scanning tunnelling microscopy / microscope

Solid state lighting

DFT	density functional theory
EL	electroluminescence
IL	ionic liquid
ITO	indium tin oxide
LCD	liquid crystal display
LEC	see LEEC
LED	light-emitting diode
LEEC	light-emitting electrochemical cell
OLED	organic light-emitting diode

PEDOT:PSS	poly(3,4-ethylenedioxythiophene) : poly-styrenesulfonate
PL	photoluminescence
RGB	red, green, blue
SSL	solid state lighting
$t_{1/2}$	time from voltage turn-on to the time where the luminance is half of the maximum value
$t_{1/5}$	time from voltage turn-on to the time where the luminance is one fifth of the maximum value
t_{on}	time to reach the maximum luminance

Abstract

The theoretical background for this thesis is given in **Chapter 1**. It covers the field of supramolecular chemistry including the phenomena of self-assembly, the history and synthesis of dendrimers, the concept of coordination chemistry and the chemistry of iridium, the history and principles of the scanning tunnelling microscope (STM), and the theory and applications of solid state lighting, especially of the light-emitting electrochemical cells (LEECs).

The background chapter is followed by a short introduction to the materials, methods, and instruments used in this thesis (**Chapter 2**).

In the following two chapters, the syntheses of achiral and chiral Fréchet dendrimers (**Chapter 3**) and the subsequent reactions to the achiral and chiral Fréchet dendronised 2,2'-bipyridine ligands (**Chapter 4**) are described. Additionally, for most of the compounds presented in these chapters, the monolayer behaviour on graphite was studied with STM. For example, for 3,5-bis(dodecyloxy)-phenylmethanol, a very highly resolved image could be detected and detailed considerations of the adopted monolayer could be performed. Chirality was introduced into the molecules for the purpose of altering the preference for a particular conformation, as it has been shown before by *L. Scherer*[1] that these type of ligands tend to adopt different conformations when adsorbed on graphite. Unfortunately, the measurements of the chiral ligands did not reveal any significant information. Therefore, no detailed discussion of the conformations in the monolayer could be given. Nevertheless, in a monolayer of the diastereomeric mixture of 4,4'-bis(1-(3,5-bis(dodecyloxy)-phenyl)propoxy)-2,2'-bipyridine, two clearly differing patterns could be observed which were attributed to different stereoisomers.

Chapter 5 deals with the synthesis of dendrons decorated with perfluorinated alkyl chains and their use in the functionalisation of 2,2'-bipyridine ligands. Adsorbed monolayers on graphite of such a ligand were studied with STM. Due to a, apparently, lower propensity to establish monolayers, only few examples of visualised patterns could be observed.

The following three chapters cover the synthesis and STM-visualisation of 2,2'-bipyridine-based ligands (**Chapter 6**), their iridium(III) complexes (**Chapter 7**), and the use thereof in LEEC devices (**Chapter 8**). In **Chapter 6**, simple and more advanced ligands were synthesised and characterised. In the case of the ligands which were functionalised with dendrons presented in **Chapter 2**, STM studies of monolayers on graphite are discussed. **Chapter 7** presents the synthesis and characterisation of iridium(III) complexes obtained from ligands described in the previous chapter. The characterisation comprises measurements of NMR, MS, UV-Vis, photoluminescence, electrochemistry, and, where single crystals could be obtained, their solid state structures. For the complexes bearing dendronised ligands, STM measurements were performed which revealed highly resolved patterns. In the last chapter (**Chapter 8**), results from LEEC devices fabricated with complexes described in **Chapter 7** are shown. The device preparation and the measurement of their characteristics were performed by the group of *H. Bolink* who kindly allowed the publication of their results in this thesis. It could be shown that for all complexes exhibiting an intramolecular π-π stacking, the stability of their devices was increased dramatically.

This thesis has brought together the realms of chemical design with, firstly, studies of the physical behaviour of the envisioned molecules on the surface and, secondly, systematic structural optimisation of iridium(III) complexes for the application in solid state lighting. With the work presented in this thesis, a major breakthrough for long-lived LEECs has been achieved allowing lifetimes of several thousands of hours, an increase of several orders of magnitude compared to the best-performing devices reported to date (see **Chapter 1** and **Chapter 8**).

Chapter 1

Background

1.1
Supramolecular chemistry

1.1.1
History and terminology

For more than 180 years, since urea was synthesised by *F. Wöhler*,[2] molecular chemistry has developed a vast array of highly sophisticated and powerful methods for the construction of ever more complex molecular structures by the making or breaking of covalent bonds between atoms in a controlled and precise fashion.[3] Organic synthesis grew rapidly, leading to a whole series of brilliant achievements. Molecular chemistry has established its power over the covalent bond. Beyond molecular chemistry there lies the field of *supramolecular chemistry*, the goal of which is to gain control over the intermolecular bond.[3]

In contrast to molecular chemistry, the area of *supramolecular chemistry* is still a young one.[4] The term "*supramolecular*" can be traced back at least to 1925.[5] The roots of *supramolecular chemistry* are found in early discoveries, mostly in the field of biological chemistry, amongst there are molecular recognition (1894, *E. Fischer*)[6], the concept of receptors (*P. Ehrlich*)[7], and coordination chemistry (by *A. Werner*, see **Section 1.3**)[8] which would be, at least partially, regarded as *supramolecular chemistry* nowadays. With these three concepts, fixation, recognition, and coordination, the foundations of *supramolecular chemistry* are laid.[3] The term "*Übermoleküle*" was used in the mid-1930's to describe entities of higher organisation, such as the dimer of acetic acid, resulting from the association of coordinately saturated species.[9-11]

Nevertheless, the field of *supramolecular chemistry*, as we know it, started with the selective binding of alkali metal cations by crown ethers[12, 13] and cryptands[14-16]. The concept and term of *supramolecular chemistry* were introduced by *J.-M. Lehn* in 1978.[17] Earlier, *supramolecular chemistry* was defined as organised entities of higher complexity resulting from the association of two or more chemical species held together by intermolecular forces, not by covalent bonds.[18] But the use of covalent bonds to describe interactions is unhelpful, as it mixes interactions that are energetically different.[19] Furthermore, metal ligand bonds or hydrogen bonds can be substantial and strong.

A grander view of *supramolecular chemistry* focuses on the controlled assembly of multiple chemical components. The assembly can involve standard intermolecular interactions, and/or metal coordination. One broad goal is to have the ability to mimic the structure and the function of the assemblies of molecular biology.[19]

Currently, the term "*supramolecular*" has three different meanings:[19]
(a) intermolecular interactions;
(b) applied coordination chemistry;
(c) a strategy of controlled organisation of multiple separate components.

In order to disentangle this confusion, *I. Dance* recommended to use "*intermolecular*" as the adjective for the well-known weak and long interactions between molecules, and to describe elabo-

rate coordination complexes and polymers unambiguously with the terminology of coordination chemistry (see **Section 1.3**). He suggested restricting the use of the adjective "*supramolecular*" to the philosophies and strategies of grand assembly.[19]

To sum up, *supramolecular chemistry* is commonly defined as chemistry "beyond the molecule", as chemistry of tailor-shaped intermolecular interaction. In *supramolecules*, information is stored in the form of structural peculiarities. Moreover, not only the combined action of molecules is called *supramolecular*, but also the combined action of characteristic *parts* of one and the same molecule.[4]

1.1.2 Weak chemical bonds

Supramolecular chemists often use the terminology of chemical bonds (see **Section 1.1.1**). This raises the question of a definition of a chemical bond.

L. Pauling defined in 1939 a chemical bond as follows: "We shall say that there is a chemical bond between two atoms or two groups of atoms in case that forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent chemical species."[20] *Pauling* explained that this definition was meant to include not only the directed valence bond of the organic chemist but also electrostatic bonds (*e.g.* present in the solid state of sodium chloride) or even the weak bond which holds together the two O_2 molecules of O_4.[21] But he did not consider the weak van der Waals forces between molecules as leading to chemical bonding.[22]

Therefore, we will classify bonds into weak bonds (such as hydrogen bonds or π-π interactions, see below) or strong bonds (covalent bonds, coordination bonds). One has to bear in mind though, that in supramolecular chemistry, multiple ligands on one entity bind simultaneously to multiple receptors on another, therefore the understanding of the concept of *multivalency*[23-27] is important. Multivalent interactions tend to be much stronger than the corresponding monovalent ones.[21] The binding of two molecules, both having multiple recognition sites, may occur with an affinity greater than the sum of the corresponding monovalent interactions, a phenomenon that has been defined as the *cluster effect*.[28]

In the following two sections, two interactions playing a major role in supramolecular chemistry are briefly explained.

1.1.2.1 Hydrogen bonding

The hydrogen bond is the most important of all directional intermolecular interactions.[29] A hydrogen bond is the attractive force between, classically, one electronegative atom and a hydrogen

covalently bonded to another electronegative atom.[30] It results from a dipole-dipole force with a hydrogen atom bonded to nitrogen, oxygen or fluorine. The energy of a hydrogen bond (typically 5 – 30 kJ mol^{-1}) is comparable to that of weak covalent bonds (155 kJ mol^{-1}),[31] and "strong" charge-assisted or resonance-assisted X–H···Y (X, Y = O, N) show bond energies of up to 150 kJ mol^{-1}.[32] Unsurprisingly, these bonds can occur intermolecularly or intramolecularly.

As an extrapolation of this type of interaction, the involvement of weak, "unconventional", or "non-classical" hydrogen bonds has been invoked.[22] It has become almost routine to discuss and analyse intermolecular interactions in terms of C–H···O, C–H···N, C–H···F, C–H···Cl, C–H···π (see **Section 1.1.2.2**), and Cl···Cl intermolecular "bonds".[29, 33-35] It is clear that the atoms that come into contact in these intermolecular interactions are not those in the molecular interiors but those on the peripheries.[22] One cannot deny that these weak intermolecular atom–atom bonds can be neatly categorised on the basis of geometrical, spectroscopic, and even energetic criteria and are thus according to these criteria existent rather than non-existent, provided one is prepared to accept a continuum of energies until nearly zero. The question is not whether weak hydrogen bonds "exist" but rather to what extent are they relevant in distinguishing one possible crystal structure from another.[22]

1.1.2.2
π-π Interactions

Strong attractive interactions between π-systems have been known for over half a century.[36] Two different geometries of π-π stacking are observed in crystal structures, and are depicted in **Figure 1.1**.

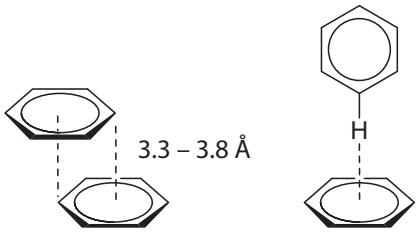


Figure 1.1 Two different possibilities of π-π stacking. Left: face-to-face geometry showing the typical range in distance.[37] Right: edge-to-face geometry.

These interactions control such diverse phenomena as the vertical base-base interactions which stabilise the double helical structure of DNA,[38] the intercalation of drugs into DNA,[38, 39] the packing of aromatic molecules in crystals,[40] the tertiary structures of proteins,[41] the conformational preferences and binding properties of polyaromatic macrocycles,[42] complexation in many host-guest systems,[43] and porphyrin aggregation.[44] To date, no readily accessible or intuitive model has been suggested to explain the experimental observations. Full *ab initio* calculations have been carried out for a limited number of small systems[45] and these do reproduce the experimental re-

sults well, but they do not explain the basic mechanisms of π-π interactions in a way that is helpful or predictive for the practical chemist. *C. A. Hunter* and *J. K. M. Sanders* presented a pictorial model and the rules they derived from it have a general applicability. In essence, the model indicates that the geometries of π-π interactions are controlled by electrostatic interactions but that the major energetic contribution occurs when the attractive interactions between π-electrons and the σ-framework outweigh unfavourable contributions such as π-electron repulsion (**Figure 1.2**).[36] Therefore, it is rather a π-σ attraction than a π-π electronic interaction which leads to favourable interactions. In face-to-face arrangements (**Figure 1.1**), offset geometries are often observed which can be explained with this model (**Figure 1.2**).

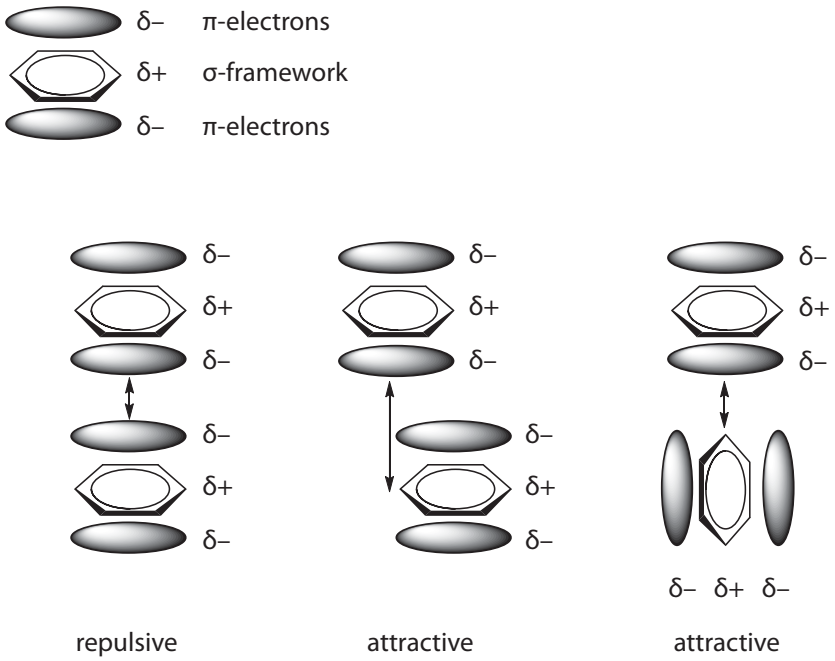


Figure 1.2 Attractive and repulsive arrangements of π-systems.[36] In this model, the π–σ attractions determine the geometry.

Nevertheless, the real origins of π-π stacking are still unclear.[46] In a recent article, *S. Grimme* pointed out that π-π stacking is a widely held misconception.[47] In his article, *Grimme* investigated the true origin of π-π stacking and questioned if it really exists. After all, many intermolecular interactions can equally well be explained with conventional dispersion forces which arise from statistical fluctuations in electron density.

In a series of computations, *Grimme* compares a group of aromatic compounds with their saturated all-trans counterparts with respect to intermolecular separation and stabilisation energy.

In summary, he recommended to use the term "π-π interactions" with care. For systems with about ten carbon atoms or less, there is little theoretical evidence for a special role of the π-orbitals. Thus, the term "π-π stacking" should be used as a geometrical descriptor of the interaction mode in unsaturated molecules and to understand π-π interactions as a special type of electron correla-

tion (dispersion) effect that can only act in large unsaturated systems when they are spatially close, which is only possible in the stacked orientation.

1.1.3 Self-assembly

Molecular self-assembly is a strategy for nanofabrication that involves designing molecules and supramolecular entities so that shape-complementarity causes them to aggregate into desired structures.[48] Self-assembly has a number of advantages as a strategy. Firstly, it carries out many of the most difficult steps in nanofabrication, those involving atomic-level modification of structure using the very highly developed techniques of synthetic chemistry. Secondly, it draws from the enormous wealth of examples in biology for inspiration. Self-assembly is one of the most important strategies used in biology for the development of complex, functional structures. Thirdly, it can incorporate biological structures directly as components in the final systems. Fourthly, because it requires the target structures to be the thermodynamically most stable ones open to the system, it tends to produce structures that are relatively defect-free and self-healing.[49-53]

One area in which self-assembly can emerge are the self-assembled monolayers (SAM).[54] There, the self-assembling process takes place in only two dimensions, *i.e.* on a surface of, for example, being gold, copper or graphite. These monolayers are well suited to measurements with scanning probe techniques (see **Section 1.4**), such as atomic force microscopy (AFM) or, as used in this thesis, scanning tunnelling microscopy (STM).

There is considerable potential for the study of structural questions of chemical interest using these new methods. Conventional three dimensional methods of determining molecular conformation such as single-crystal X-ray crystallography or NMR spectroscopic methods give structures averaged over some 10^{15} molecules. Without any averaging procedure, single molecules can be detected by analysis of surface molecular conformation of two dimensional arrays. For a better resolution, the images can be processed by averaging over 10 – 200 molecules (see also **Chapter 2**).

Dendrimer-functionalised heterocycles, such as 4,4'-bis(3,5-bis(octyloxy)benzyloxy)-2,2'-bipyridine (**14**, see **Chapter 4**) are ideally suited for the formation of SAMs[1, 55-57]. One reason is that the four octyl chains undergo intermolecular interactions between molecules, and molecules and the graphite surface. Although this interaction is quite weak (the adsorption energy per CH_2 group is about –12 kJ mol^{-1}),[58] it is however accumulated over every CH_2 group of the four octyl chains in the molecule. Another reason is the occurrence of π-π stacking of the aryl groups with the graphite surface. This interaction is also weak, but taken over the surface as whole, it is adequate to enable self-assembly to occur.

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]

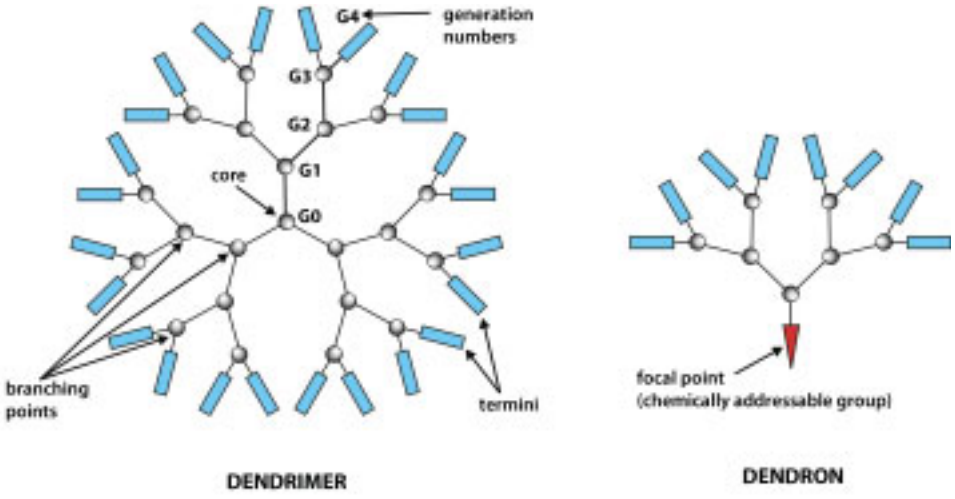


Figure 1.3 Terminology used for dendrimers. Figure based on an image which was published under public domain licensing.[65]

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 reac-

tive 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]

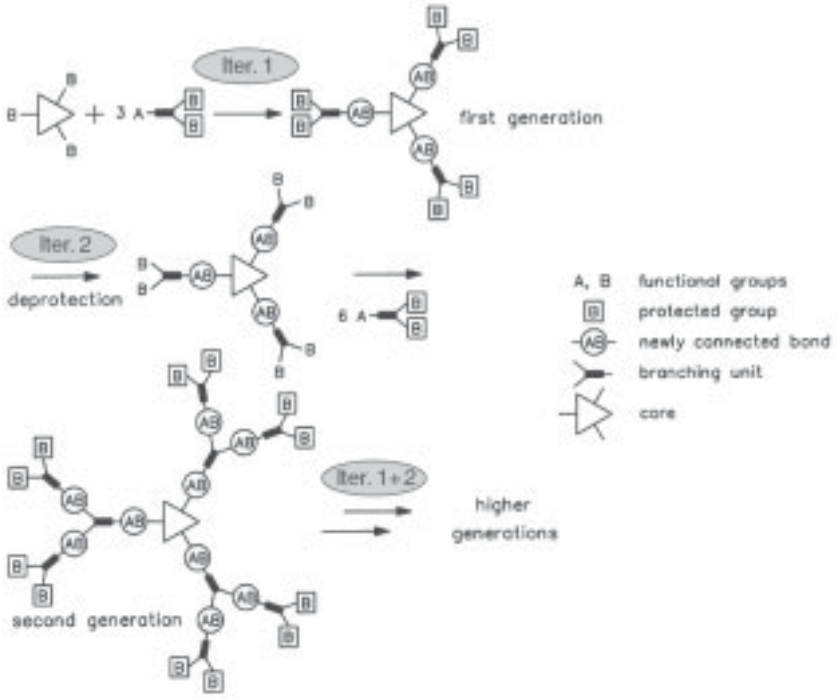
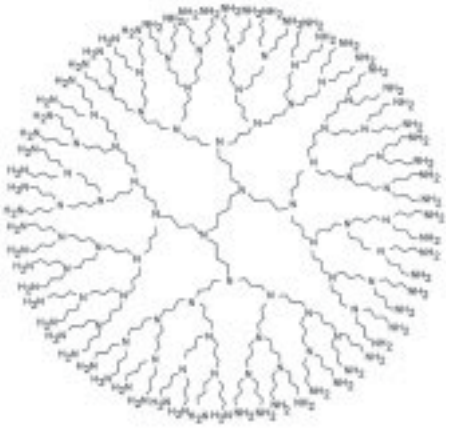


Figure 1.4 Divergent-iterative synthetic pathway for the preparation of dendrimers. Figure taken from literature.[64]

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]

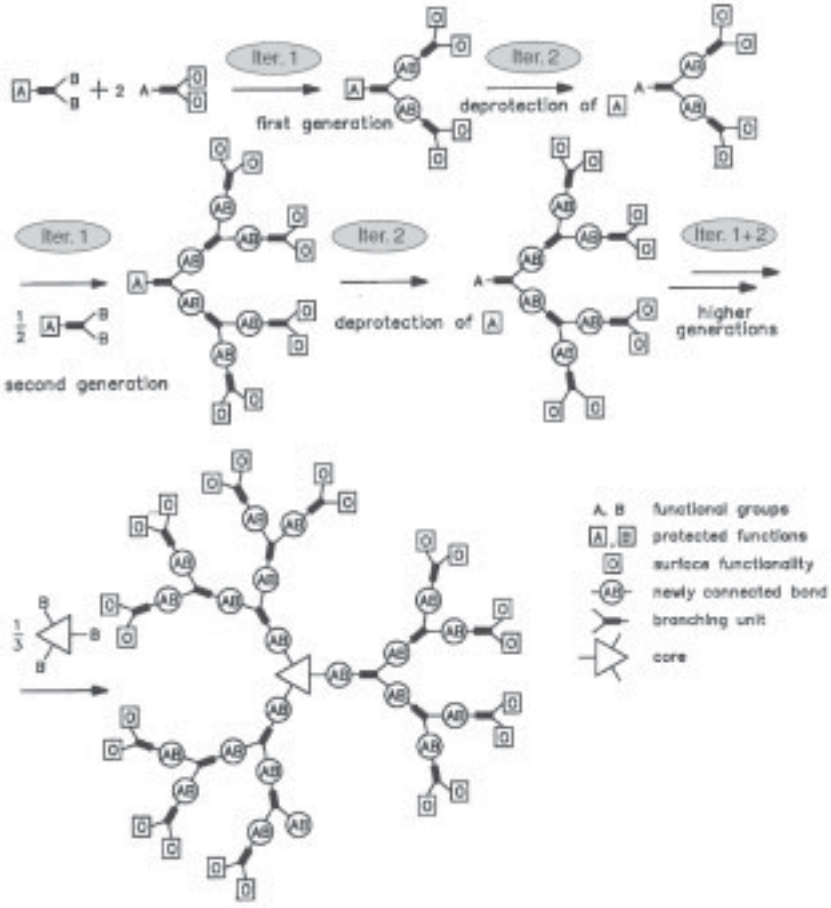


Figure 1.5 Convergent-iterative synthesis of dendritic molecules. Figure taken from literature.[64]

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