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Introduction

Since 1987, when J.-M. Lehn, C. J. Pedersen, and D. J. Cram were honored with the Nobel prize for their results in selective host-guest chemistry [1–3], supra-molecular chemistry has become a well-known concept and a major field in today's research community. This concept has been delineated [4] by Lehn: "Supramolecular chemistry may be defined as 'chemistry beyond the molecule', bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces." Self-recognition and self-assembly processes represent the basic operational components underpinning supramolecular chemistry, in which interactions are mainly non-covalent in nature (e.g., van der Waals, hydrogen-bonding, ionic, or coordinative interactions); thus, these interactions are weaker and usually reversible when compared to traditional covalent bonds. Nature presents the ultimate benchmarks for the design of artificial supramolecular processes. Inter- and intramolecular non-covalent interactions are of major importance for most biological processes, such as highly selective catalytic reactions and information storage [5]; different non-covalent interactions are present in proteins, giving them their specific structures. DNA represents one of the most famous natural examples, where self-recognition of the complementary base pairs by hydrogen bonding leads to the self-assembly of the double helix. Starting with the development and design of crown ethers, spherands, and cryptands, modern supramolecular chemistry represents the creation of well-defined structures by self-assembly processes [6] (similar to Nature's well-known systems [7]).

One of the most important interactions used in supramolecular chemistry is metal-ligand coordination. In this arena, chelate complexes derived from *N*-hetero-aromatic ligands, largely based on 2,2′-bipyridine and 2,2′:6′,2″-terpyridine (Figure 1.1), have become an ever-expanding synthetic and structural frontier.

Bipyridine has been known since 1888 when F. Blau first synthesized a bipyridine-iron complex [8]. One year later, it was again Blau who synthesized and analyzed bipyridine by dry distillation of copper picolinate [9]. Since this parent molecule consists of two identical parts, no directed coupling procedure is required for its construction. Therefore, unsubstituted and symmetrically substituted, in particular 4,4′-functionalized, bipyridines are readily accessible in good yields by simple coupling procedures. Apart from this, bipyridine metal complexes [10] (in
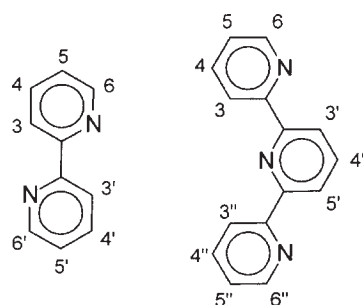
Figure 1.1 Structures of 2,2′-bipyridine and 2,2′:6′,2″-terpyridine.

particular ruthenium complexes) have very interesting photochemical properties making them ideal candidates for solar energy conversion [11].

The chemistry of 2,2′:6′,2″-terpyridines (designated as simply terpyridine or tpy; its other structural isomers are duly noted and will not be considered further here) is much younger than that of 2,2′-bipyridines. In the early 1930s, terpyridine was isolated for the first time by Morgan and Burstall [12, 13], who heated (340 °C) pyridine with anhydrous $FeCl_3$ in an autoclave (50 atm) for 36 h; the parent terpyridine was isolated along with a myriad of other *N*-containing products. It was subsequently discovered that the addition of Fe(II) ions to a solution of terpyridine compounds gave rise to a purple color giving the first indication of metal complex formation. Since this pioneering work was performed, the chemistry of terpyridine remained merely a curiosity for nearly 60 years, at which point its unique properties were incorporated into the construction of supra-molecular assemblies. The number of publications dealing with terpyridine has risen sharply as shown in the histogram (Figure 1.2) – a trend that is predicted to continue, since it is a pivotal structural component in newly engineered constructs based on metallo-polymers and crystal engineering.

The terpyridine molecule contains three nitrogen atoms and can therefore act as a tridentate ligand [14, 15]. It has been extensively studied as an outstanding complexing ligand for a wide range of transition metal ions. The ever-expanding potential applications are the result of advances in the design and synthesis of tailored terpyridine derivatives. The well-known characteristics of terpyridine metal complexes are their special redox and photophysical properties, which greatly depend on the electronic influence of the substituents. Therefore, terpyridine complexes may be used in photochemistry for the design of luminescent devices [16] or as sensitizers for light-to-electricity conversion [17, 18]. Ditopic terpyridinyl units may form polymetallic species that can be used to prepare luminescent or electrochemical sensors [19, 20]. In clinical chemistry and biochemistry, functio-nalized terpyridines have found a wide range of potential applications [21], from colorimetric metal determination [22, 23] to DNA binding agents [24–26] and anti-tumor research [27–29].

Terpyridines have also been utilized for catalytic purposes [30, 31] and in asymmetric catalysis [32]. Another interesting application regarding novel
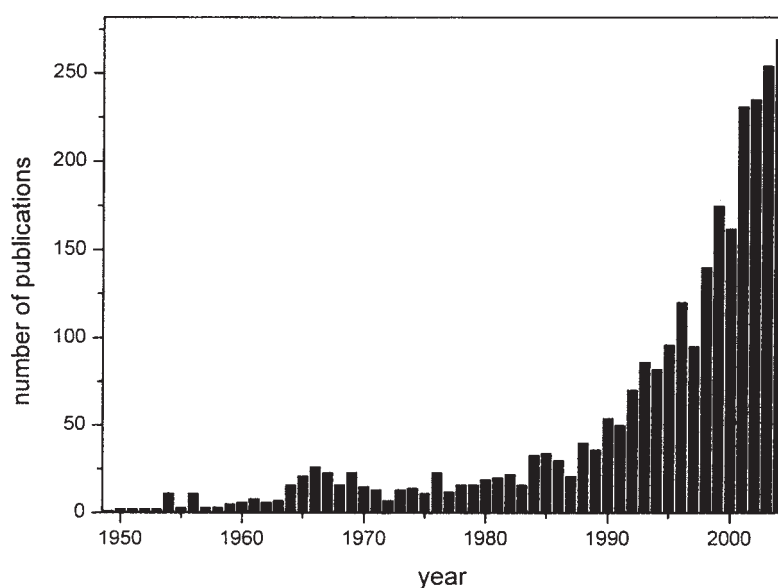
Figure 1.2 Histogram of the number of publications containing the term "terpyridine" using SciFinder (search performed 10.05.2005).

supramolecular architectures is the formation of "mixed complexes", where two differently functionalized terpyridine ligands are coordinated to a single transition metal ion [33–35]. One of the most promising fields for new terpyridine compounds is their unique application in supramolecular chemistry [36]. In this context, the formation of supramolecular terpyridine containing dendrimers [4, 37–41] can be pointed out. Layer-by-layer self-assembly of extended terpyridine complexes on graphite surfaces forms grid-like supramolecular structures [42–45]. Self-assembly of terpyridine compounds on gold [46], CdS [47] or TiO$_2$ [48], as well as surface functionalization with specially functionalized terpyridine ligands [49], should also be mentioned in this context. Terpyridines, incorporated in macromolecules, enable well-defined supramolecular polymer architectures to be formed, opening up the opportunity of "switching" within physical and chemical properties of materials [34, 35, 50–55].

In view of the notable importance of 2,2′:6′,2″-terpyridine ligands and their metal complexes in the current research, we herein focus on architectures containing this ligand and the corresponding metal complexes. Therefore, this book is divided into topics featuring different architectures and concepts containing terpyridine metal complexes.

Chapter 2 summarizes the known synthetic strategies leading to different terpyridines. Since 4′-substituted terpyridine currently represents the most valuable family of derivatives, emphasis is directed toward the routes to its synthesis.

Chapter 3 describes the preparation and properties of terpyridine metal complexes. Emphasis will be on *bis*terpyridine-Ru(II) complexes and their optical

properties as well as related dyads and triads. Other metal(II) complexes could potentially act as "molecular switches", thus opening up avenues to the construction of nano-devices.

Chapter 4 features various supramolecular aggregates composed of terpyridine-metal subunits, ranging from grids to cyclic structures; moreover, special complexes, where terpyridine complexes are combined with fullerenes or biochemical groups, are described.

Chapter 5 presents polymeric architectures containing terpyridine systems with various architectures, ranging from side-chain-functionalized polymers via main-chain metallopolymers to biopolymers.

Chapter 6 addresses metallodendrimers, micelles, and resins, representing approaches to nanoreactors and immobilized novel catalysts.

Chapter 7 describes catalysis using surface-modified terpyridine metal complexes, opening up potential utilitarian applications, such as assemblies and layers capable of behaving as photoactive materials for use in organic solar cells and LEDs.

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