CRITICAL REVIEW

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Recent developments in the supramolecular chemistry of terpyridine–metal complexes

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This *critical review* describes recent developments in the field of supramolecular chemistry of terpyridine–metal complexes. The synthesis and characteristics of single as well as multiple homo- and heterometallic complexes is discussed. Furthermore, complexes containing fullerenes, biological building blocks, extended aggregates of different architectures as well as rings are presented. A special emphasis is placed upon the properties (*e.g.* redox properties, luminescence *etc.*) of functional systems. Potential applications in optical nano-devices, molecular storage units, molecular switches and solar cells are discussed.

Introduction

Supramolecular chemistry has become one of the most interesting fields in modern chemistry. In 1987, J.-M. Lehn, C. J. Pederson and D. J. Cram received the Nobel Prize for their pioneering work.[1] Self-recognition and self-assembly processes represent the basic concept of supramolecular chemistry and the interactions involved are mainly of a non-covalent nature (*e.g.* van der Waals, hydrogen bonding, ionic or coordinative interactions). Compared to covalent bonds, these interactions are weaker and usually reversible. Nature is the model for 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;[2,3] different non-covalent interactions are present in proteins, giving them their specific structures. DNA represents one of the most famous examples, where the self-recognition of the complementary base-pairs by hydrogen bonding leads to the self-assembly of the double helix. Today, many synthetic supramolecular systems are known.[1,4] The resulting compounds are expected to reveal new chemical and physical as well as biological properties. Starting from biomimetic systems, the concept was extended to "molecular machines"[5] and supramolecular polymers.[6]

Among the approaches to supramolecular polymers is the use of self-complementary multiple hydrogen bonding units that are characterized by increased stability compared to single hydrogen bonds.[7–13] Supramolecular assemblies and fully reversible polymers have already been prepared in the past. Another type of interaction, which has been used extensively in supramolecular chemistry, is metal coordination. In particular, chelating ligands are of interest, since they allow the construction of defined supramolecular architectures and possess an increased stability compared to hydrogen bonding. Besides bipyridines,[14] terpyridines have been utilized extensively.

Terpyridines were first discovered by Morgan and Burstall.[15] By heating pyridine with anhydrous iron(III) chloride at 340 °C in an autoclave (50 atms.) for 36 hours, 2,2′:6′,2″-terpyridine was produced (besides bipyridines and other products). It was subsequently discovered that the addition of iron(II) ions to a solution of terpyridine compounds gave rise to a purple color, giving the first

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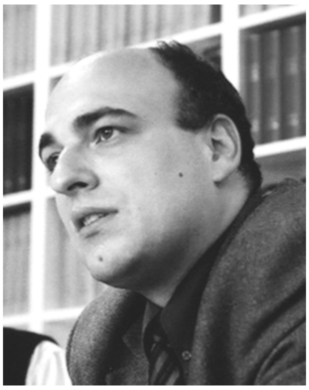
Harald Hofmeier


Ulrich S. Schubert

Ulrich S. Schubert was born in 1969 and obtained his PhD in 1995 with Prof. Eisenbach at the Universität Bayreuth (Germany) in cooperation with Prof. Newkome at the University of South Florida (USA) investigating the synthesis and morphologies of bipyridine-containing macromolecules. During his postdoctoral time with Prof. Lehn at the Université Strasbourg (France) he worked on inorganic grid-like systems. After that he moved to the Technische Universität München (Germany) to obtain his habilitation (1999) in chemistry working on metallo-supramolecular assemblies and polymers (with Prof. Nuyken). From 1999 to 2000 he held a temporary position as a professor at the Center for NanoScience at the Universität München (Germany). Since June 2000 he has been a full professor (chair of Macromolecular Chemistry and Nanoscience) at the Eindhoven University of Technology.

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indication for the formation of a metal complex. In the following sections, an overview of the synthesis of various functionalized terpyridine ligands (especially 4′-functionalized terpyridines) is given, followed by a description of the latest achievements in the field of terpyridine complexes, ranging from mononuclear complexes *via* dyads and triads (in this section, emphasis is directed towards ruthenium(II) complexes and their optical properties) to extended supramolecular architectures. In this contribution, only 2,2′:6′,2″-terpyridine and its complexes are discussed; the ligand is therefore abbreviated to "terpyridine".

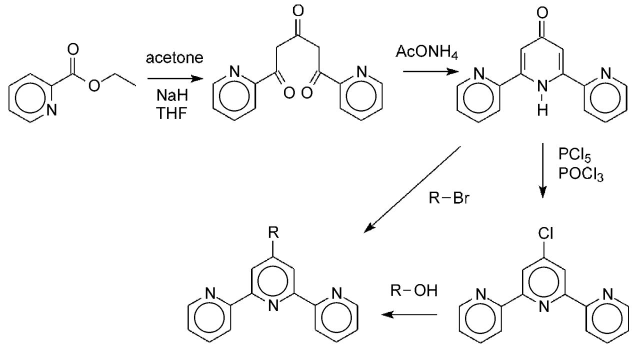
Synthetic strategies

Terpyridine ligands

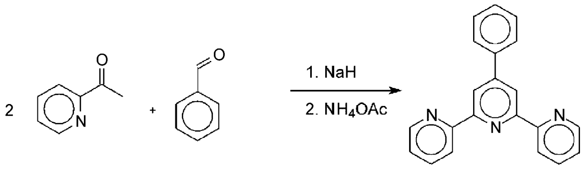
Terpyridine–ruthenium complexes of the type $[Ru(tpy)_2X_2]$ (X = *e.g.* Cl^-, ClO_4^-, PF_6^-) are already well-known.[16,17] A main characteristic is the strength of the metal–ligand coordinative bond in these complexes. With many transition metal ions in low oxidation states a bis-complex is formed, with pseudo octahedral coordination at the metal center. The stability of this type of complex can be explained by the strong metal–ligand (d–π*) back donation. Furthermore, a strong chelate effect is present. The common geometry of this type of complex is a distorted octahedral geometry, because the most common coordinativity for transition metal ions is hexacoordination. The distorted octahedral coordination geometry has been determined in detail by X-ray structure analysis.[18]

A variety of terpyridines, functionalized at different positions, has been prepared over the past years. Several reviews were published on the subject.[19,20] Therefore, only a short overview from the most common functionalization procedures to the most frequently used 4′-functionalized terpyridines, including some recent publications, will be presented in this contribution.

4′-Functionalized terpyridines are versatile building blocks for supramolecular assemblies and polymers. Whereas asymmetrically functionalized bipyridines (*e.g.* bipyridines bearing a substituent on one pyridine ring) may lead to isomers (*fac* or *mer* tris(bipyridine) diastereomers), depending on the orientation of the functional groups (*facial* or *meridional*) upon complexation with metal ions, the complexation of terpyridines leads to defined complexes because of a 4′-functionalized terpyridine possessing C_{2v} symmetry with a rotation axis through the 4′-position. Numerous examples are known for the reaction between 4′-chloro(terpyridine) and alcohols in DMSO, using a base catalyst, *e.g.* KOH (Scheme 1).[21–23]

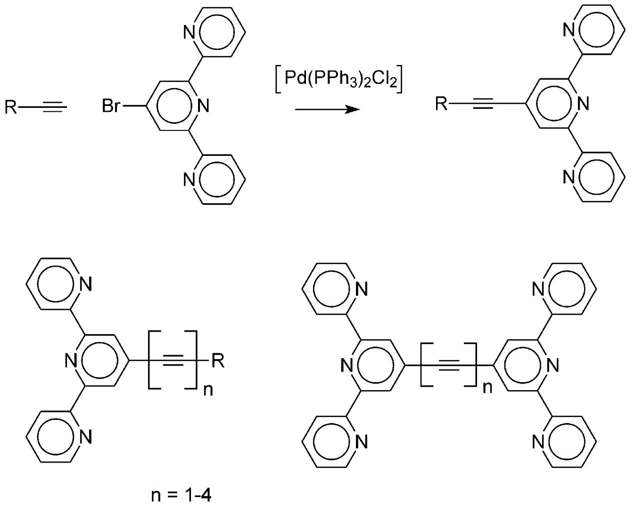


Scheme 1 Synthetic approach to 4′-functionalized terpyridines *via* the pyridone[26–28] and chloro(terpyridine)[21–23] route.



Scheme 2 Synthesis of 4′-phenylsubstituted terpyridines.[17,29]

Moreover, pyridone[24,25] (the precursor of 4′-chloro(terpyridine)) can be utilized for functionalization.[26,27] For this type of reaction, bromides or tosylates are used as starting materials to react with the pyridone. More examples are presented in a recent publication,[28] where a nitrile, an epoxide and various other moieties containing an olefinic group could also be introduced in one step. 4′-Phenyl groups can be introduced by reacting acetopyridine with benzaldehyde (Scheme 2) in a so-called "Kröhnke" condensation reaction.[17,29] The cross-coupling of alkynes with bromo-terpyridines is straightforward and opens avenues to various polytopic terpyridine ligands that can be employed in the construction of supramolecular assemblies (Scheme 3). Due to the extended conjugation systems, these compounds are characterized by outstanding optical properties such as room temperature luminescence of the corresponding ruthenium complexes. Furthermore, they might be used as "nanowires". A large variety of these compounds has been prepared in the laboratory of R. Ziessel, who reviewed this topic in 1999.[30] This reaction is very versatile and allows the construction of a large variety of mono- and bis(terpyridines) containing extended conjugated alkyne units.



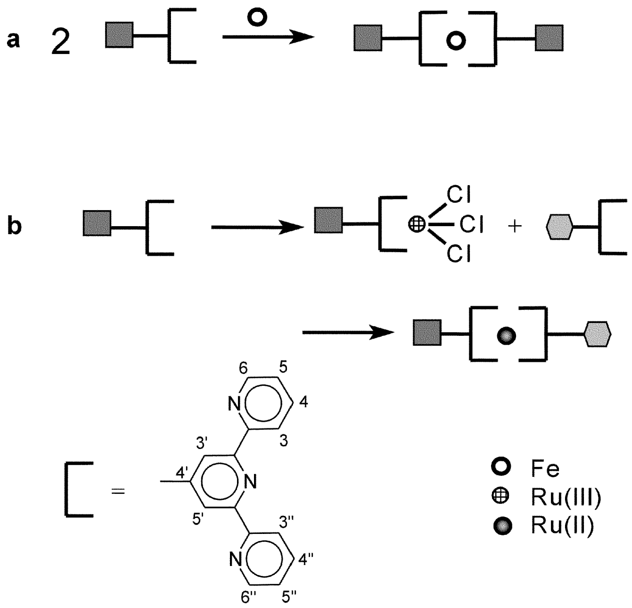
Scheme 3 Palladium-catalyzed cross-coupling of alkyne derivatives.[30]

Metal complexes

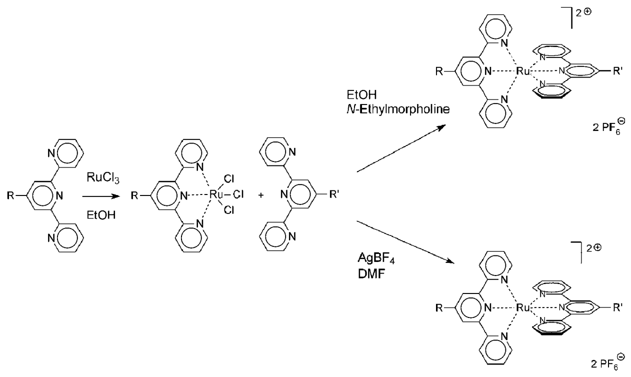
In order to obtain bis(terpyridine) metal complexes, metal ions (*e.g.* zinc(II), cobalt(II), copper(II), nickel(II), iron(II)) are usually treated with the respective ligand in a 1 : 2 ratio (Scheme 4a). The complexes are subsequently purified by exchange of the counterions and recrystallization of the complex. Addition of metal salts to a mixture of two different terpyridines leads to a statistical mixture of homo complexes and the hetero complex. In order to prepare exclusively asymmetric complexes, a directed strategy, where the two ligands are introduced in a two-step reaction (*via* a mono-complex intermediate, Scheme 4b) has to be used. Suitable metals for this strategy are ruthenium and osmium.

Ruthenium complexes. Complexation of terpyridine ligands to a ruthenium(II) center can be carried out in a two-step reaction (Scheme 5). The ruthenium(III) intermediate is subsequently reacted in the second step under reductive conditions to yield the corresponding asymmetric ruthenium(II) complex.[17]

In the first step, ruthenium(III) trichloride hydrate is added to a methanolic or ethanolic solution of the first terpyridine ligand. The resulting mono-complex is poorly soluble in most cases and can be simply isolated by filtration. Subsequently, this intermediate is suspended with the second ligand in methanol, containing *N*-ethylmorpholine[31] and refluxed for 1–4 hours. The solvent also acts



Scheme 4 Schematic representation of the formation of terpyridine complexes.



Scheme 5 Synthetic strategy towards asymmetric terpyridine complexes.[17,32]

as a reductive agent to reduce the ruthenium(III) to ruthenium(II), followed by loss of the chlorides and eventual coordination of the second terpyridine.

Alternatively, an equimolar amount of silver tetrafluoroborate is added to the ruthenium(III) mono-complex in DMF or acetone to remove the chlorides.[32] The vacant coordination sites are now occupied by the weakly binding solvent molecules, thereby activating the ruthenium(III) complex. Unlike terpyridine ruthenium(III) trichloride that is reacted in suspension, the activated species is soluble. This intermediate is reacted without isolation with the second terpyridine (after filtration of the formed silver chloride) which leads to the desired bis(terpyridine) ruthenium(II) complex. Yields between 50% and 90% can usually be obtained. Although this is a direct method, the formation of a statistic mixture of hetero and homo complexes has been reported in one specific case,[33] but this atypical behavior could not be explained by the authors.

In another method for end-capping functionalized terpyridines with terpyridine ruthenium(II) fragments, Ru(tpy)(DMSO)Cl$_2$ is employed for the synthesis of asymmetric complexes.[34] Another, somewhat unusual method, was presented by D. Greene *et al.* who showed that microwave-assisted heating gave the desired product in yields of up to 94% within one minute.[35]

Symmetric terpyridine complexes can be obtained by the RuCl$_3$-*N*-ethylmorpholine method, either in a two-step reaction by applying the same ligand twice or in a one-pot reaction.

Another method described by Rehahn starts from ruthenium trichloride, which is de-chlorinated with AgBF$_4$ in acetone.[36] The resulting hexaacetone ruthenium(III) complex, where the ligands are loosely bound, is reacted with the ligand, which involves a reduction.

It has to be noted that the ruthenium(II) center can be reduced by electrocrystallization to result in neutral complexes. A crystal structure could be obtained, showing indeed only the neutral bis(terpyridine)–ruthenium complexes without any other ions.[37] The observed species consists of ruthenium(II) ions coordinated to two terpyridine radical anions.

Photo-physical properties. Absorption as well as emission spectra reveal that a metal–ligand charge transfer takes place in terpyridine–ruthenium complexes. As opposed to bipyridine complexes, where phosphorescence phenomena can be observed over a wide temperature range, no emission is detected at room temperature in the case of terpyridines due to a non-radiative transition of the excited triplet metal to ligand charge-transfer (^{3}MLCT) state *via* a triplet metal-centered (^{3}MC) state to the ground state (see *e.g.* ref. 16). However, at low temperatures, this path becomes less efficient, and therefore luminescence could be observed.[38–40] For a sufficient observation of the emission properties, the material can be "dissolved" in a rigid glass at 77 K.[41]

The photo-physical properties of the complexes can be fine-tuned by the introduction of donor, acceptor or both kinds of groups, leading to room temperature luminescent terpyridine–ruthenium(II) complexes. Another method to improve the luminescence lifetime and quantum efficiency utilizes the attachment of aromatic groups. One of the first examples is represented by 4′-*p*-tolyl(terpyridine); an extension of this approach of connecting aromatic rings to the terpyridine moiety lead to 4,4′,4″-triphenylterpyridine, which revealed further improved optical properties. For more detailed information on these kinds of systems, the reader is referred to a review by Balzani and Sauvage *et al.*[16]

A very different approach to the preparation of room temperature luminescent ruthenium complexes is the entrapment of the compounds in zeolite cages.[42] The zeolite-induced destabilization of the ligand–field (LF) state resulted in a strongly enhanced room temperature emission of the terpyridine–ruthenium(II) complex.

A feature article by Armaroli highlights photo-physical processes in various metallo-supramolecular compounds, including energy and electron transfer processes.[43]

Other luminescent metal complexes. Iridium(III) ions were found to show an enhanced luminescence behavior compared to their ruthenium(II) analogues.[44] Lifetimes above 1 μs could be obtained, which were assigned to be predominantly ligand–centered π–π^* phosphorescence emissions.[45] Furthermore, asymmetric complexes could be synthesized in a similar fashion as ruthenium(II) complexes: IrCl$_3$ hydrate can be reacted with terpyridine ligands to form an iridium(III) mono-complex. This intermediate is subjected to the second ligand without changing the oxidation state of the metal center, but under harsher reaction conditions (diethylene glycol at 200 °C). Among the examples are complexes containing both a tolyl and a pyridyl group, the latter was subsequently converted into a methylpyridinium group. The luminescence of these complexes is quenched in the presence of chloride ions, making such systems interesting as sensors.[46] A recent contribution from Williams *et al.* describes 4′-biphenyl(terpyridine)–iridium complexes, which exhibit intense long-lived emission due to conjugation of the aromatic rings. This explanation was confirmed by a comparison to analogous complexes of 4′-mesityl terpyridine, where conjugation is completely hindered because of steric repulsion.[47]

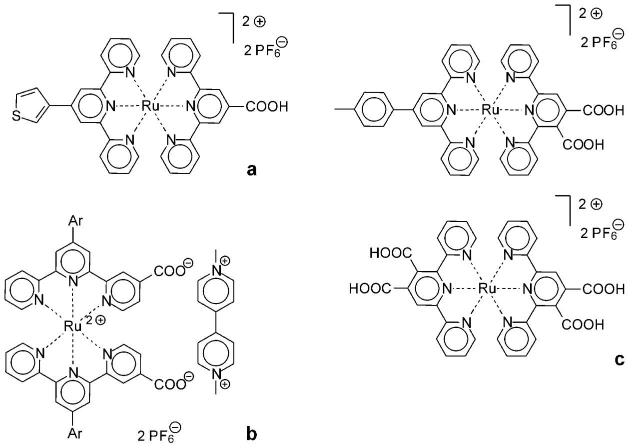
Iridium complexes bearing porphyrins and cyclodextrins are described in a later section. For a recent review on iridium systems, see also ref. 48.

Osmium complexes of terpyridines are also room temperature luminescent and are described later. Another metal, leading to luminescent species, is platinum, which forms [terpyridine–PtCl]$^+$ type complexes. Whereas the parent complex is non-luminescent at room temperature, complexes of 4′-substituted terpyridines or different co-ligands are emitters. The DNA-binding properties of these complexes makes them interesting as sensors in biochemistry.[49]

Uninuclear terpyridine ruthenium complexes

A lot of work has already been done in the field of terpyridine complexation chemistry. Still, a significant amount of research is being performed on uninuclear terpyridine complexes. A huge potential lies in these compounds regarding the fine-tuning of optical properties or the use as precursors for supramolecular architectures.

Carboxy groups (Scheme 6) play an important role as substituents on terpyridine ligands due to their potential use as an anchoring group on surfaces. One example is TiO_2, which is widely used in solar cell applications.[50] Terpyridine–ruthenium complexes, attached to TiO_2, could be used as sensitizers in novel solar cells. In the reported example, an electropolymerizable thienyl group has also been introduced into the terpyridine complex (Scheme 6a):[51] $[RuLL'][PF_6]_2$ (L = 4′-(3-thienyl)-2,2′:6′,2″-terpyridine; L′ = 4′-carboxy-2,2′:6′,2″-terpyridine) was prepared following two different synthesis pathways. The first one involves a protection of the carboxylic group on the ligand before formation of the complex, followed by hydrolysis in the final step. This route was chosen because the direct complexation of the free carboxylic acid resulted in a very low yield. The second approach is a new route, based on oxidation of a furan ring: 4′-(2-furyl)terpyridine was reacted with 4′-(3-thienyl)terpyridine ruthenium trichloride, followed by treatment of the resulting complex with $KMnO_4$ under basic conditions which leads to the carboxy compound. For the latter case, an even higher yield compared to the first route was obtained.

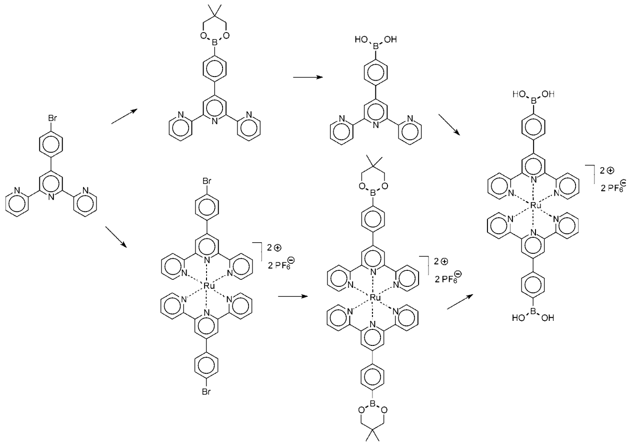


Scheme 6 Carboxy-functionalized terpyridine complexes.[51–53]

Carboxy-groups have also been introduced into the 4-position of terpyridines (Scheme 6b).[52] Due to their spatial orientation, they can easily coordinate to methyl viologen (4,4′-bis(methylpyridinium) by ionic interactions, providing a photo-induced electron transfer.

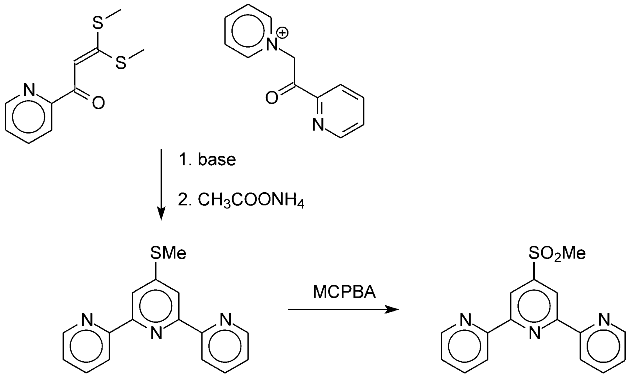
In order to increase the electron injection efficiency and to reduce the chance of desorption of the complexes from the TiO_2 surface, asymmetric bis(terpyridinyl)–ruthenium(II) complexes carrying vicinal carboxylic acids were developed (Scheme 6c).[53] Because the complexation of the free di-acid resulted in the loss of one carboxylic group (decarboxylation), a protection of the acid groups by ester-formation was necessary. The resulting compounds showed room temperature luminescence and efficient sensitization of nanocrystalline TiO_2 films, with conversion yields (IPCE) of up to 70%.

A new versatile method for the preparation of functionalized terpyridines and their corresponding metal complexes utilising boron chemistry was investigated.[54] In the following example 4′-(4-bromophenyl)terpyridine and 4′-bromoterpyridine have been functionalized with boronate groups by a palladium-catalyzed Miyaura cross-coupling, resulting, in the first example, in a boronate ester-functionalized terpyridine (Scheme 7). Subsequent hydrolysis of this intermediate led to the free boronic acid. The ligand, bearing the boronic ester, could be complexed with ruthenium(II), while the free acid disintegrated because of the destabilized boron bond. Furthermore, the boronation could also be performed on a preformed ruthenium(II) complex. The resulting boronate complexes are interesting starting materials for further reactions involving the boronate group (*e.g.* Suzuki–Miyaura cross-couplings).



Scheme 7 Synthesis of boronate–terpyridine complexes.[54]

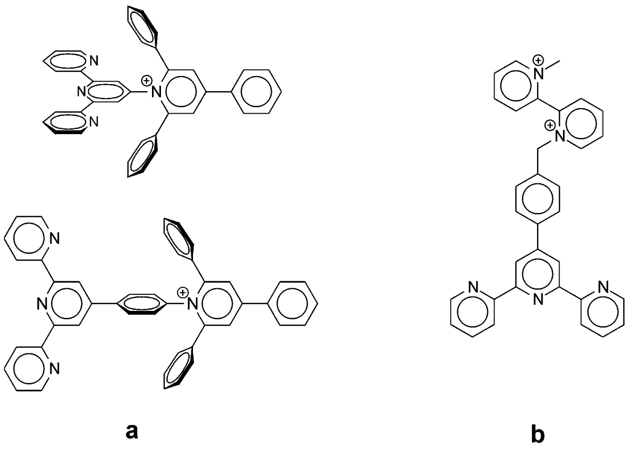
Electron withdrawing groups in the 4′-position of terpyridines have been shown to result in room temperature-phosphorescent ruthenium(II) complexes.[31] Chloroterpyridine revealed a weak luminescence. In order to obtain a more efficient complex, a methylsulfone group was introduced *via* a methylthio terpyridine, followed by oxidation (Scheme 8).[55] The intermediate was prepared according to the Potts method[56] and oxidized to the sulfone using a per-acid.



Scheme 8 Synthesis of a terpyridine sulfonate.[55]

Another acceptor moiety that has been reported recently is a triphenylpyridinium group.[57] Due to the steric demands of the aromatic rings, there is no conjugation of the whole system. Furthermore, rotation around the molecular axis is inhibited (Scheme 9a). In spite of the lack of conjugation between the terpyridine and the triphenyl pyridinium moiety (due to the bulky phenyl rings), an enhanced room temperature luminescence was observed.[58] This behavior was ascribed to a through-bond electronic substituent effect originating from the directly connected electron-withdrawing group. In the case where the unit is separated by a *para*-phenyl ring, the formation of photo-induced electron-transfer (PET) processes with the formation of charge-separated (CS) states is possible.

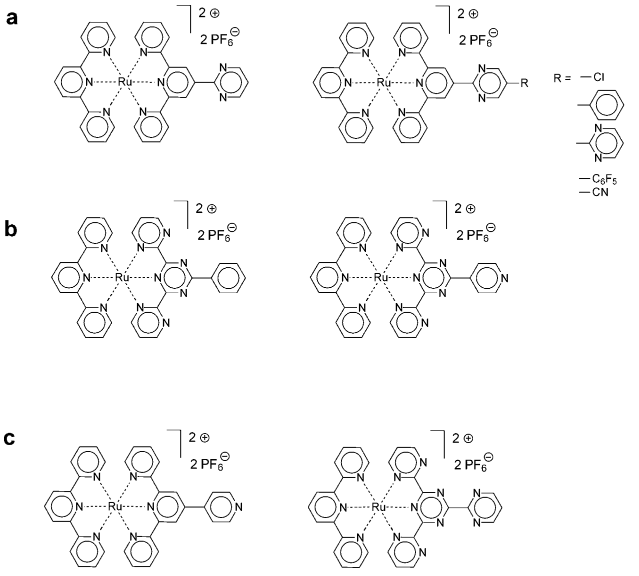
Another example, where a pyridinium moiety is connected to a terpyridine, is shown in Scheme 9b. In this case, a 1-methyl-1′-



Scheme 9 (a) Triphenylpyridinium[58] and (b) viologen[59] functionalized terpyridine ligands.

[4-(2,2′:6′,2″-terpyridin-4-yl)benzyl]-4,4′-bipyridinediium was used to prepare an osmium complex, where the characteristic osmium luminescence is efficiently quenched by the viologen moiety. The quenching most probably involves an intramolecular electron transfer.[59]

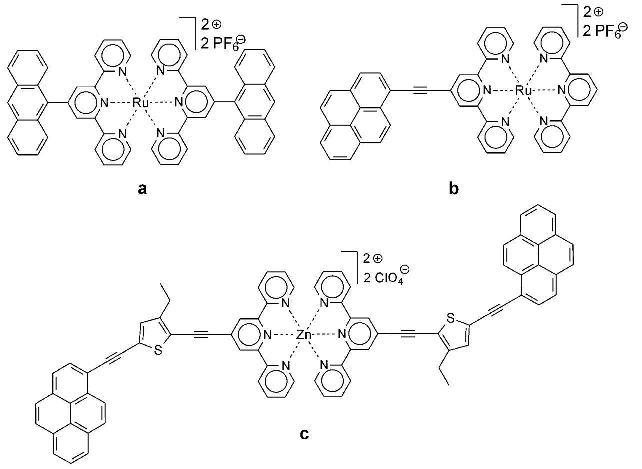
Besides the introduction of electron-withdrawing groups, the extension of the conjugated π-system of the ligand by one or more aromatic rings is also a promising approach (Scheme 10). One strategy towards such systems is the use of connected benzoic aromatic rings. In the case shown in Scheme 10a, a pyrimidine moiety has been introduced into the 4′-position of a terpyridine.[60] In addition, analogous terpyridines bearing a second pyrimidine, phenyl or pentafluorophenyl group in the *p*-position of the first aromatic ring, have been prepared to extend the conjugated π-system. This configuration leads to an increase in the gap between the metal-center and the MLCT states. A luminescence at room temperature (lifetime up to 200 ns) is the result. Other examples of luminescent ruthenium complexes include complexes involving the ligand 2-(4′-pyridyl)-4,6-bis-(2′-pyridyl)-1,3,5-triazine. The bis(2′-pyrimidyl)-1,3,5-triazines can be considered as "heteroterpyridines" (nitrogen atoms are in the 3,3′,5′,3″-positions), which have the potential for room temperature luminescence (Scheme 10b).[61] Similar ruthenium(II) complexes of 4′-pyridyl and 4′-pyrimidyl functionalized terpyridines and *N*-hetero-terpyridines have been prepared and characterized in the group of J. A. Thomas (Scheme 10c).[62] Despite the similarity to the previously described systems, the authors reported that these complexes are non-luminescent.



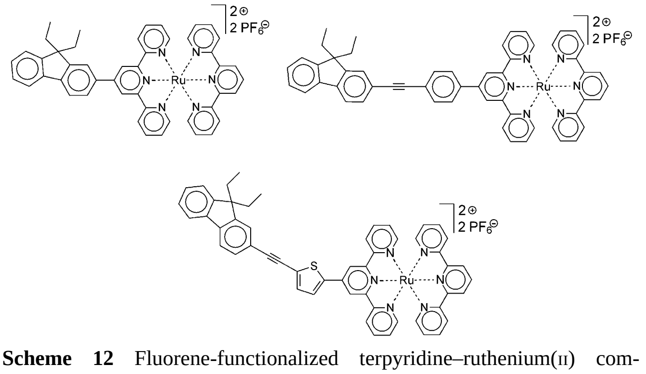
Scheme 10 Phenyl and pyridyl functionalized complexes of (hetero)-terpyridines.[60–62]

An interesting feature of the 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine ligand is that it is actually composed of three terpyridine subunits, the reported complex thus contains two vacant complexing units. This architectural feature makes this system interesting for the construction of supramolecular assemblies as described later.

Besides benzoic aromates, annellated or fused aromates have also been introduced into terpyridines, where the corresponding ruthenium complexes show the ability for room temperature luminescence. Among the examples is a terpyridine bearing an anthracene in the 4′-position, which has been complexed to form ruthenium(II) and iron(II) complexes.[63] Other examples include the introduction of pyrene moieties (Scheme 11).[64] Recently, ethynyl–pyrene units have also been introduced in the 5,5″-positions of a terpyridine.[65] Moreover, pyrene moieties have been linked *via* a bis(ethynyl)thiophene bridge to the terpyridine.[66] This ligand is luminescent at room temperature due to the efficient population of an intramolecular charge transfer excited state. However, addition of zinc(II) ions results in quenching of the emission, making such systems interesting as "sensors" for metal ions. Furthermore, alkyne cross-coupling reactions have also been used to obtain fluorene-functionalized terpyridine complexes.[67] Fluorene units have been coupled to terpyridines directly or *via* phenylene–ethynylyne or thiophenyl–ethynylyne connectors, applying Kröhnke synthesis and Sonogashira coupling reactions. The ruthenium(II) complexes, formed from these ligands, are shown in Scheme 12. These ruthenium complexes are non-luminescent despite the attached conjugated groups, whereas the corresponding zinc complexes are highly luminous.

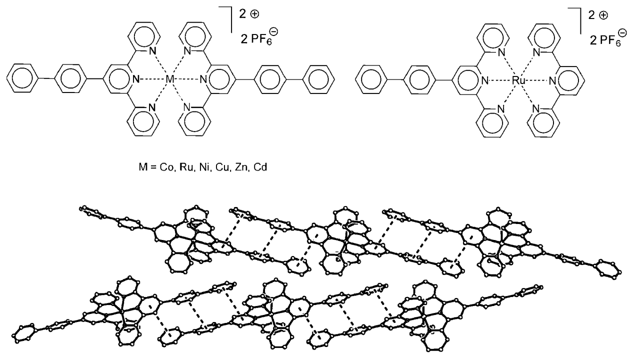


Scheme 11 Terpyridine–ruthenium complexes, containing extended aromatic functions (a) anthryl,[64] (b) pyrene-1-ylethynyl[65] and (c) 4-ethyl-5-pyren-1-ylethynylthiophen-2-ylethynyl.[66]



Scheme 12 Fluorene-functionalized terpyridine–ruthenium(II) complexes.[67]

Besides photo-physical properties originating from delocalization phenomena, the intermolecular interactions of such compounds are also of interest. Extended aromatic systems are known to give rise to π–π interactions, which could be relatively strong for large molecules. Such π-stacking could be exploited for the 3-dimensional arrangement of terpyridine complexes (Scheme 13).



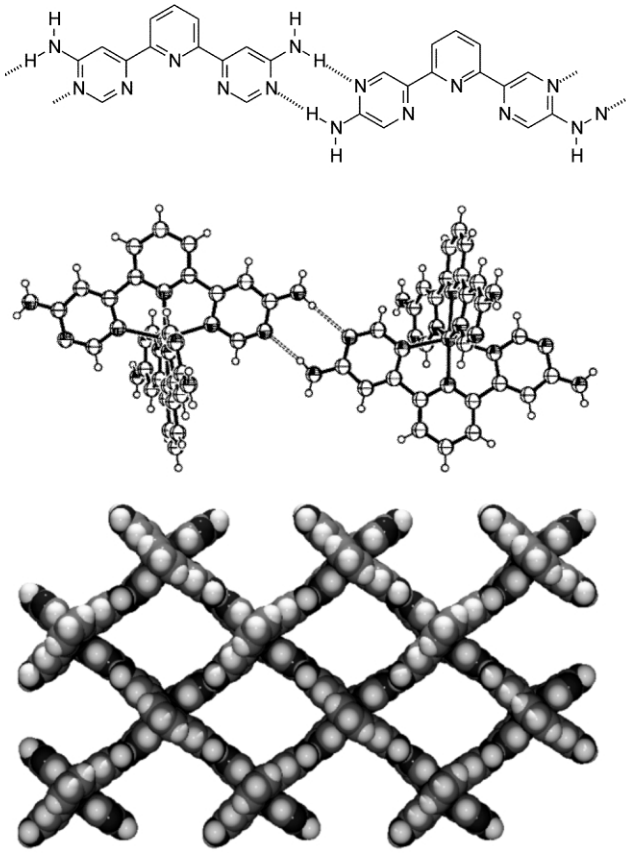
Scheme 13 π-Stacking of 4′-(4-biphenyl)terpyridine–ruthenium complexes.[68]

The group of Alcock reported the synthesis of 4′-biphenyl functionalized terpyridines and the preparation of the corresponding complexes using a variety of metal ions.[68] Furthermore, a ruthenium complex with one biphenyl-terpyridine and one unfunctionalized terpyridine was synthesized. π-Stacking interactions between the biphenyl and pyridyl rings were observed in the crystal structure, resulting in aggregation of the complexes in the solid state. Depending on the metal ion, different structures were found: for cobalt, ruthenium, nickel and copper, biphenylene–biphenylene interactions lead to linear rod-like arrays; for complexes of zinc and cadmium, biphenylene–pyridyl interactions lead to two-dimensional sheets. Moreover, ruthenium, zinc and cadmium complexes showed room temperature luminescence both in solid state as well as in solution.

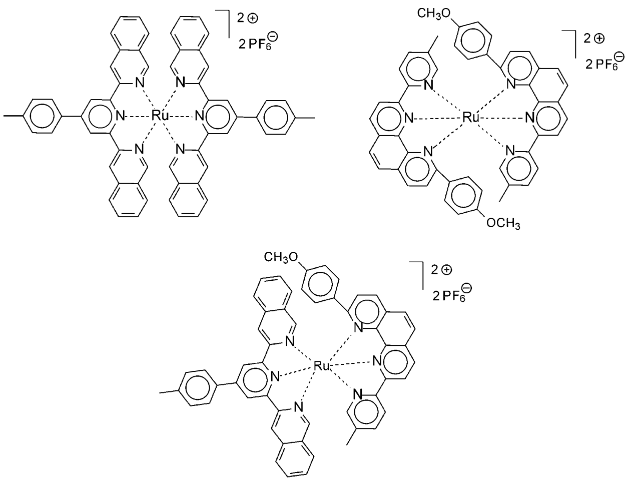
Another non-covalent interaction, which has been used in the chemistry of terpyridine complexes, is hydrogen bonding. In one particular example, two “heteroterpyridines”, containing amino–pyrimidine and amino–pyrazine moieties, have been synthesized, which could form double hydrogen bonds.[69] The solid-state structures did indeed reveal the formation of extended grid-like structures through molecular recognition (Scheme 14). Whereas PF_6 counter-ions of a cobalt complex resulted in a complete saturation of the hydrogen bonds, BF_4 counter-ions led to partially broken networks. With zinc triflate, only half of the bonds are formed, leading to a chain-like assembly. An explanation is the different packing of the complexes in the crystal, influenced by the size of the respective counter-ions. These complexes could be considered as a prototype for the generation of novel organized arrays of terpyridine complexes through sequential self-assembly processes.

Numerous differently functionalized terpyridine analogues, where pyridine rings have been replaced by quinoline and phenanthroline moieties, have been used to form symmetric as well as asymmetric complexes.[70] Besides functional groups, connected by σ-bonds in various positions, fused phenyl rings were also introduced (Scheme 15). Among the species described is also a “terpyridine” consisting of a pyridylphenanthroline. Moreover, cyclo-metallated species have been prepared.[70] Here, one *N*-atom is replaced by carbon, resulting in a Ru–C bond. Some of these complexes show long MLCT excited state lifetimes (70–106 ns) at room temperature.

With a view to applications in solar cells or artificial photosynthesis, photosensitizer–electron acceptor systems have been prepared by connecting a naphthalene–diimide moiety to a terpyridine unit (reaction of the corresponding aminoterpyridines with the naphthalene anhydride) and subsequent formation of the corresponding ruthenium complexes. Unsubstituted terpyridine as well as 4′-*p*-tolyl(terpyridine) have been applied as the second ligand and the acceptor unit has been attached in a rigid fashion *via* a phenylene group or *via* an additional saturated carbon atom (Scheme 16a).[71] However, unlike the corresponding bipyridine complexes, no electron transfer was detected in the case of the terpyridine complexes, which was ascribed to the short lifetime of the excited state of the ruthenium–terpyridine complex.



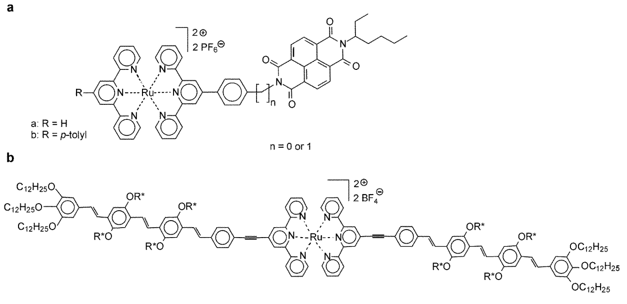
Scheme 14 Terpyridines with hydrogen bonding groups that assemble to a grid-like superstructure. *Reprinted with permission from* ref. 69 © *2000 Wiley-VCH.*



Scheme 15 Ruthenium complexes of terpyridines with fused aromatic rings.[70]

Oligo(*p*-phenylene vinylene) (OPV) is of special interest due to its outstanding optical properties. Furthermore, it is known to act as a donor in an efficient photo-induced electron transfer, which is of interest for solar cell applications. In combination with fullerene compounds acting as acceptors, the photochemical generated charges could be separated and drained with suitable compounds.

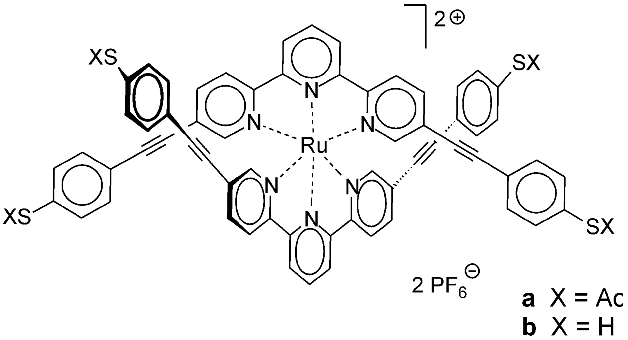
In order to improve this system, two OPV units bearing terpyridine ligands (synthesized by a palladium-catalyzed cross-coupling reaction), have been converted to a ruthenium(II) complex (Scheme 16b).[72] Near steady-state photo-induced absorption



Scheme 16 Naphthalenediimide-^{71} and oligo(*p*-phenylene vinylene)^{72}-substituted terpyridine complexes.

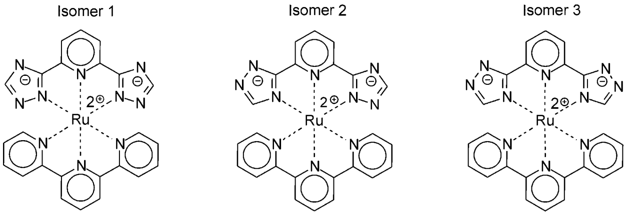
experiments did indeed reveal a charge-separated state, which was dependent on the polarity of the solvent. In further experiments, the OPV donor has been coupled directly to a fullerene *via* terpyridine–ruthenium complexation.

Ruthenium complexes containing fully conjugated ligands terminated with thiol groups (substitution in the 5,5″-position) have been obtained by cross-coupling of the corresponding alkynes. The resulting compounds could subsequently be immobilized on gold surfaces (Scheme 17). Self-assembled monolayers of single molecules have been imaged using scanning tunnelling microscopy.^{73} The delocalized phenylene–ethynyl moiety could act as molecular wire, which might eventually lead to applications in molecular electronics.



Scheme 17 Conjugated thiol terpyridine complex.^{73}

There are also numerous examples where terpyridines have been combined with tridentate terpyridine analogues (Scheme 18). In the case of bis(triazole)pyridine, for example, different isomers are possible, because this ligand possesses different sets of nitrogen atoms that are able to coordinate to the ruthenium ion.^{74} Compared to $[Ru(tpy)_2]^{2+}$, the luminescence lifetime of the these systems showed a 300-fold increase and is explained by a rise of the energy of the ^{3}MC level (in contrast to the previously described examples, where the ^{3}MLCT state was lowered). Furthermore, 5-phenyl-bis(triazole) and bis(tetrazole)pyridines have been reported. The triazole rings are deprotonated in the complexes (6π-aromatic), and a reprotonation results in quenching of the emission.^{75}



Scheme 18 Different coordination isomers of the complex Ru(tpy)bis-(triazole)pyridine.^{74}

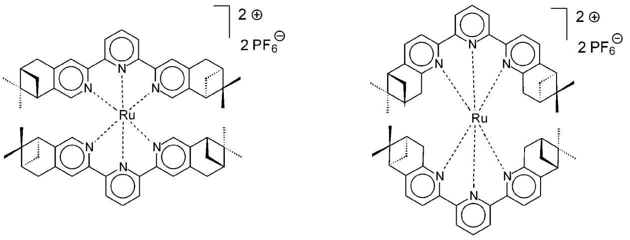
Attempts have been undertaken to prepare liquid crystals containing metal complexes in order to obtain mesophases where the characteristic properties of such complexes are incorporated. One approach to achieve this goal consists of a terpyridine–ruthenium(II) complex, bearing a long alkyl chain. $C_{19}H_{31}$ and $C_{31}H_{63}$-tails have been introduced, resulting in amphiphilic complexes, which could also act as surfactants.^{76} For the complex containing the short chain, lyotropic mesomorphism was found in water, while a similar behavior was detected for the long-chain complex in ethylene glycol.

Chiral complexes

First attempts to introduce chirality into terpyridines were undertaken by the group of Abruña *et al.*^{77} A 4′,4″″′-bis(methylthio)-4″,4″″-bis(*n*-propylthio)septipyridine was synthesized which, upon complexation with copper, forms double-helices involving two ligand moieties and two copper(II) ions. In these complexes, the ligand strands act as double terpyridine units, leaving two pyridine rings uncoordinated. The same group reported the preparation of 6,6″-diphenyl-4,4″-bis(alkylthio)-2,2′:6′,2″-terpyridines, which forms helical complexes with Cu(I) ions.^{78} In this case, the terpyridine serves as a bis-dentate and a mono-dentate ligand, whereas with Cu(II) ions, a regular terpyridine complex is formed.

Another system is described in ref. 79. In this case chirality is introduced by a 2,2-bis[2-(4(S)- or 4(R)-phenyl-l,3-oxazolinyl)]-propane that was coordinated together with unfunctionalized terpyridine to an oxo-ruthenium(IV) complex.

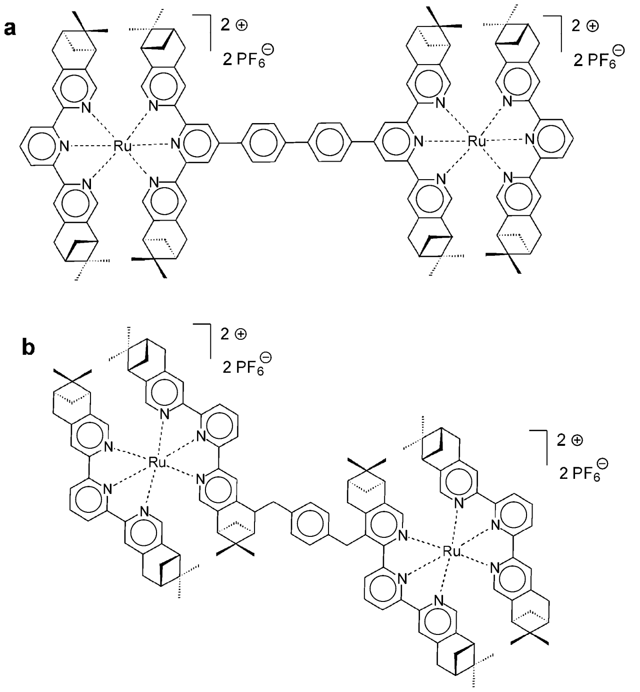
The approach of von Zelewsky consists of the utilization of a chiral ‘dipineno’-(5,6:5″,6″)-fused 2,2′:6′,2″-terpyridine ligand as well as of the analogous (4,5:4″,5″)-fused derivatives.^{33} Here, chirality is introduced by fusing a chiral pinene-cycle in 5,6-position onto the terpyridine ring, thus making the ligand itself chiral (Scheme 19). The ligands were synthesized enantiomerically pure. Circular dichroism (CD) investigations showed that the resulting complexes are helically distorted in a chiral fashion. These and other pinene-functionalized terpyridines have been investigated regarding stereoselective catalysis.^{80}



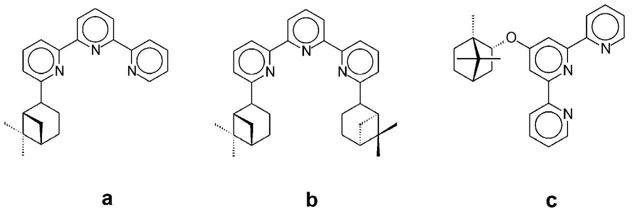
Scheme 19 Chiral terpyridine complexes with fused pinene units.^{33}

Subsequently, this work has been continued to investigate multinuclear and polymeric systems. The group of Abruña *et al.* reported the linking of two ‘dipineno’-(5,6:5″,6″)-fused 2,2′:6′,2″-terpyridine ligands in the 4′-position by a biphenyl moiety (Scheme 20a).^{81} A slightly different approach consists of the connection *via* the dipineno groups and a *p*-xylene linker (Scheme 20b). Both ligand systems have been used to obtain dinuclear ruthenium(II) complexes and coordination polymers that exhibit room temperature luminescence due to the aromatic connector. The ligands have also been applied in the preparation of iron(II) coordination polymers.^{82,83}

Furthermore, attempts were undertaken to introduce chirality in side groups, which are connected only *via* one σ-bond (instead of the previously described fused systems). Besides an example of 6,6″-substituted terpyridines (Scheme 21a–b),^{80} another example was reported by Constable *et al.*,^{84} where a bornyl group acted as the substituent in the 4′-position of the terpyridine (Scheme 21c). Ruthenium(II) as well as cobalt(II) complexes were synthesized using these types of ligands. However, transfer of chiral information to the complex core was minimal. In the group of Schubert, 4′-(3,4,5-tris(3,7-dimethyl-octyloxy)phenylethynyl)terpyridine was prepared *via* a palladium-mediated alkyne cross-coupling.^{85} Compared to the previously described systems, the distance between the chiral groups and the terpyridine is larger. CD spectroscopy of the



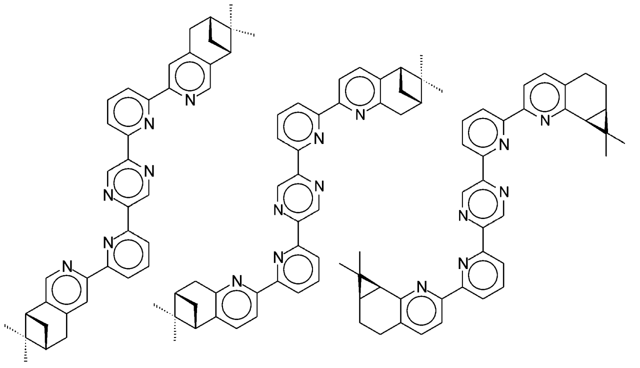
Scheme 20 Chiral terpyridine–ruthenium complex dyads.[81]



Scheme 21 Connecting a chiral unit *via* a single bond.[80,84]

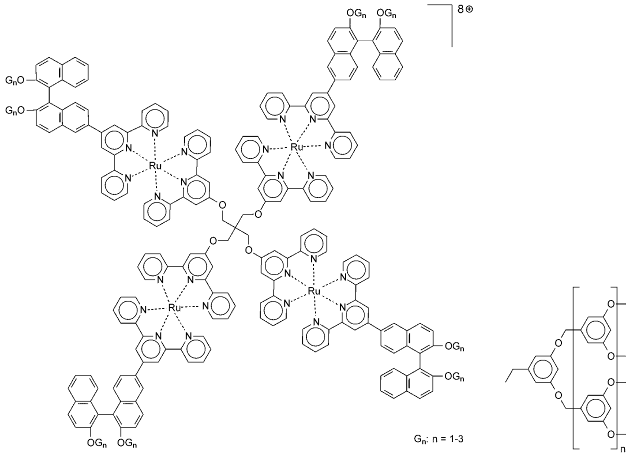
corresponding ruthenium(II) complex in an apolar solvent (dodecane) revealed chirality in the complex moiety, suggesting the transfer of chirality into the complex by aggregation. In good solvents, where the complexes are molecularly dissolved, no CD effect was found.

Novel ligands that contain a central pyrazine ring connected to peripheral bipyridine moieties have been prepared, providing terpyridine-like binding moieties.[86] The coordination sites are pointing in opposite directions. Annellated terpene fragments render these metal chelators chiral (Scheme 22). Thus, stereoselectivity is introduced into the formation of chiral, multinuclear coordination species.



Scheme 22 Bis-coordinating ligand, bearing chiral groups.[86]

An interesting extended chiral architecture was achieved by Jiang *et al.*[87,88] by the successful preparation of a chiral terpyridine–dendrimer molecule, consisting of four terpyridine–Ru(II) complexes (Scheme 23). Terpyridine groups were attached to the binaphthyl units, subsequently reacted with $RuCl_3$ and further

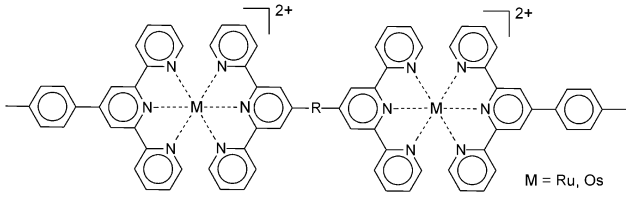


Scheme 23 Tetranuclear terpyridine–ruthenium complex, bearing chiral binaphthyl groups.[87,88]

complexed to the terpyridinyl-functionalized pentaerythrol, which acts as the dendrimer core. CD spectroscopy revealed an enantiomerically pure compound.

Dyads and triads

Many systems containing two or three terpyridine complex units, linked by different spacers, have been synthesized. Both homodyads (same metal ions) and heterodyads (different metal ions) are known. Interesting examples are represented by the combination of the metals ruthenium and osmium. A variety of such compounds and their properties was reviewed by Sauvage *et al.*[16] in 1994. The general formula is depicted in Scheme 24. If a ruthenium complex

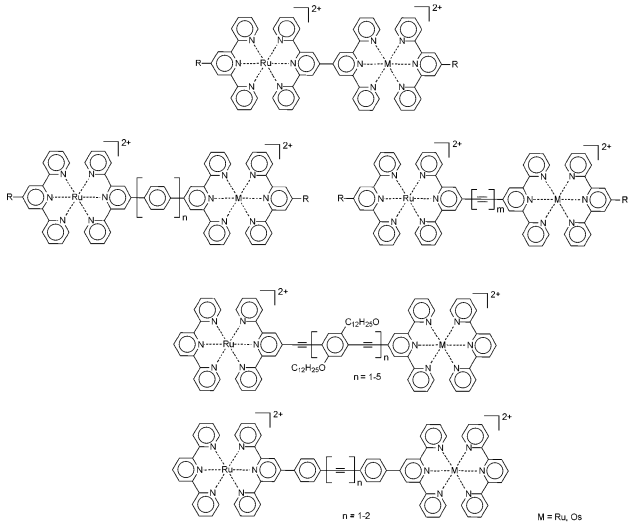


Scheme 24 Schematic representation of a dyad.

is connected to an osmium complex, then an energy transfer from Ru to Os can be observed when exciting the ruthenium(II) complex unit. Energy and also electron transfer processes make such complex-arrays interesting for use as "molecular wires". A variety of heterometallic polyads of bipyridine and terpyridine complexes are presented in a review by Barigelletti *et al.*[89] Many dyads have been synthesized using rigid bis(terpyridine) ligands. Therefore, the resulting complexes have a rod-like structure (Scheme 25).

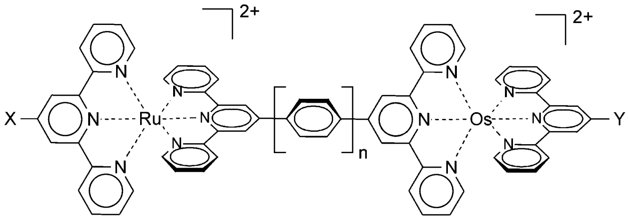
Starting from a dyad with directly connected terpyridines, various spacer groups have been introduced. Intensive work has been performed on a wide range of conjugated spacers of different length and composition, allowing the photo-physical properties of the corresponding complexes to be fine-tuned. Phenylene-linked dyads have been reviewed in ref. 16 and the alkyne-linked complexes in ref. 30. Complexes of the mixed alkyne–phenylene linked ligands have been reported more recently.[90] For the *p*-phenylene-bridged dyads (with $n = 0–2$) it has been shown that conjugation enhances the luminescence lifetime.[91] However, the phenylene-bridged system shows less luminescence than the directly linked one because the phenyl ring is not coplanar to the terpyridine moieties, which prevents complete delocalization.

Besides homometallic ruthenium complexes, ruthenium–osmium dyads have been prepared using the bridging ligands. The synthesis of these systems has been performed by first complexing only one coordinating site with a ruthenium fragment, followed by a reaction with an osmium precursor as a second step. An energy-transfer from the ruthenium center to the osmium could be observed in the products.



Scheme 25 Dyads, linked by *p*-phenylene and/or ethynyl moieties.[16,30,90,91]

The basics of the system depicted in Scheme 26 have already been reported in the literature,[16] nevertheless, a lot of research is still being carried out on this system. Further adjustment and fine-tuning of the optical properties could be achieved by introducing donor or acceptor groups into the terminal ligands.[92] Electrochemical experiments revealed both metal–metal and ligand–ligand interactions and photo-physical studies showed a very efficient energy transfer mechanism, which is most likely based on an electron exchange mechanism to be operational.



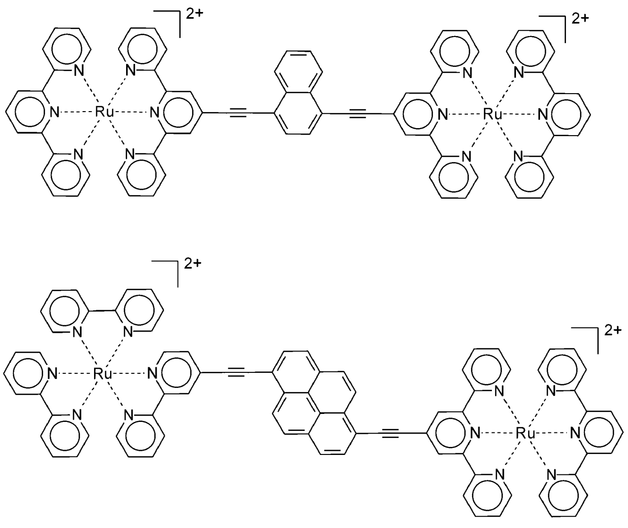
a	X = Y = phMe,	n = 0
b	X = Y = phMe,	n = 1
c	X = Y = phMe,	n = 2
d	X = SO$_2$Me, Y = H,	n = 0
e	X = SO$_2$Me, Y = H,	n = 1
f	X = SO$_2$Me, Y = phMe,	n = 1

Scheme 26 *p*-Phenylene-linked dyads with donor and acceptor groups.[16]

Architectures of terpyridine complexes, connected to ethynyl groups, are of major importance due to their enhanced photo-physical properties. Because of an enhanced delocalization of the electrons in such systems, the triplet energy state is lowered, resulting in efficient luminescence at room temperature.

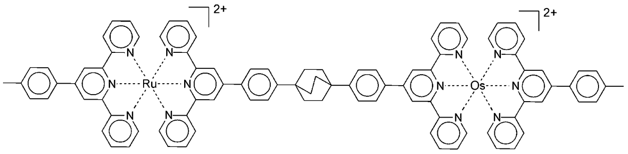
In a different experiment, rhodium(III) has been introduced into an analogous series of phenylene-bridged binuclear complexes.[93] Compared to the Ru–Os system, an energy transfer from Rh(III) to Ru(II) could be observed. In the case of direct linkage, an electron transfer from Ru(II) to Rh(III) was found. Analogous dyads have been prepared using Ru(II) and Co(III) complexes.[94] For these systems, electron transfer from ruthenium to cobalt was found.

In order to study the effect of different central aromatic units on the photo-physical properties of the dyad, naphthalene has been introduced into the backbone of the bridging ligand, which was subsequently converted to the ruthenium dyad (Scheme 27).[95] Compared to the analogous phenylene-linked dyad, the triplet lifetime is prolonged. In the same laboratory, a pyrene that connects a terpyridine–ruthenium(II) complex moiety with a bipyridine, has been reported recently.[96]



Scheme 27 Dyads, linked by various aromatic groups.[95,96]

In the dyads discussed up to now, rigidity in the spacer is maintained by conjugated systems such as aromates or alkynes. In order to investigate the effect of conjugation on the photo-physical and electrochemical properties of rod-like dinuclear complexes, a saturated bicyclic compound was introduced into the linker unit of a ruthenium(II)–osmium(II) dyad (Scheme 28).[97] In this system, the electronic interactions are completely decoupled without affecting the rigidity of the spacer. The central bicyclo[2.2.2]octane acts as an insulator between the two complex moieties, preventing electronic communication between the metal centers. Therefore, the electrochemistry of such a dyad resembles that of the isolated parent complexes. At room temperature, no energy transfer was found due to the distance of the complex units. At low temperatures (77 K) in a matrix, however, the triplet lifetime was long enough to allow an energy transfer. As expected, no electron transfer was detected due to the isolating linker.



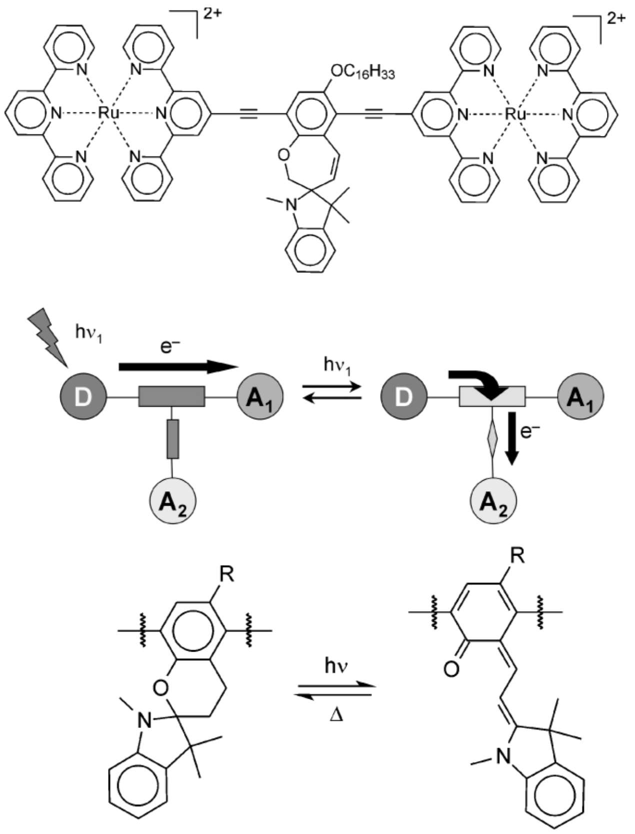
Scheme 28 Ruthenium–osmium dyad containing an insulating bicyclo[2.2.2]octane.[97]

During the process of creating molecular devices, a dyad was designed which could act as a T-junction relay (molecular switch).[98] The spiropyran moiety in the bridge undergoes light-activated ring-opening to the merocyanine form and reforms thermically. Whereas in the closed form the delocalized bridge could act as a "molecular wire" (it is known that the MLCT state involves the LUMO, which spans across both terminals), in the merocyanine form the alternative pathway to the side-group is opened (Scheme 29).

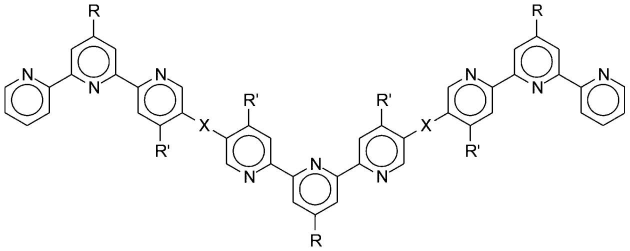
All the multinuclear complexes reported previously herein were composed of 4′-functionalized terpyridines, giving rise to rod-like complex arrays. In contrast to these approaches, the bridging ligand depicted in Scheme 30 consists of three terpyridines, which are linked in the 4- and 4″-positions. Different structures are therefore accessible.[99] Compared to the previously described tris-ligands, in this case individual terpyridine moieties are linked in the 5- and 5″-positions by ethyl and ethylene groups, respectively. Trinuclear ruthenium(II) complexes with unfunctionalized terpyridine have been synthesized, revealing luminescence at room temperature for the ethylene-linked complex and no emission for the alkylspacer-separated triad.

Switchable dyads and triads

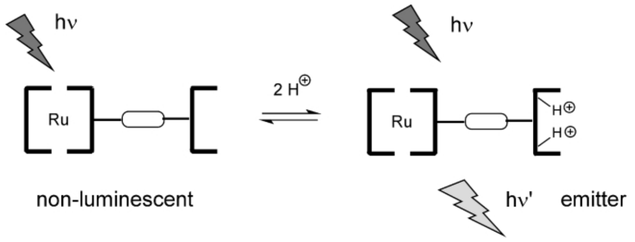
Multinuclear terpyridine complexes, especially those capable of energy and/or electron transfer, are promising compounds for



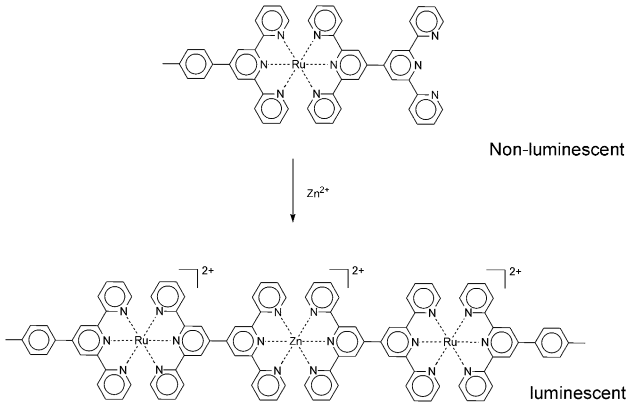
Scheme 29 Dyad, containing a spiropyrane, which could act as a molecular switch (T-junction relay) and schematic representation of the switching process.[98]



Scheme 30 Ligand for a 5,5″-linked triad.[99]



Scheme 31 Luminescence switching by protonation of a free terpyridine moiety.[100]



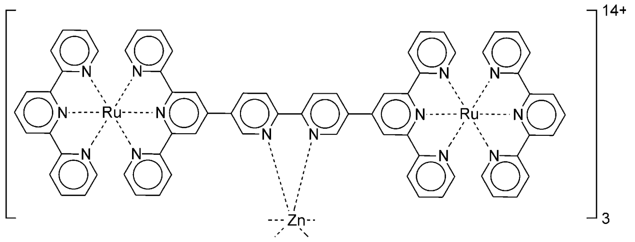
Scheme 32 Switching of luminescence by complexation with zinc(II) ions.[92]

future applications in optical nano-devices or solar cells. The field of devices and molecular switches, where electrochemical or optical activities can be switched simply and reversibly, are of special importance.

The mono-ruthenium(II) complex of a bridging ligand (separated by zero to two phenylene rings, as described in the previous references) could not only be used for further complexation, it also possesses other interesting properties. By protonation of the non-coordinating free terpyridine moiety, the luminescence properties could be modulated in a reversible manner. In this example, the non-luminescent complex became luminescent after protonation initiated by pH change, giving access to "switchable" luminescence (Scheme 31).[100] Moreover, complexes of this type can be extended further, through complexation by addition of different metal ions like iron(II) or zinc(II) to result in ABA-triads (Scheme 32). The almost non-luminescent ruthenium(II)–terpyridine chromophore, functionalized with an uncoordinated terpyridine fragment, has been complexed with Zn(II) ions, leading to a luminescent rod-like complex array revealing a luminescence enhancement factor (EF) larger than 10.[92] Due to the reversible, relatively weakly co-ordinated zinc complex, this system also gives rise to "switchable" emitters.

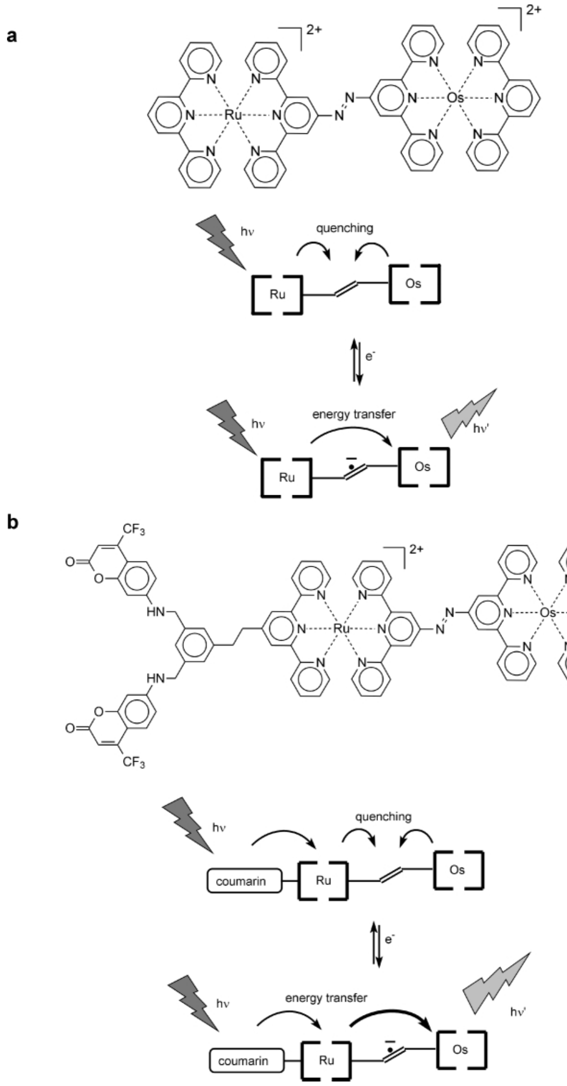
A different approach to tunable metal complex arrays includes the incorporation of a different complexing moiety such as bipyridine within the bridging ligand. One of the first compounds to be synthesized was a dyad, bridged by a 2,2′-bipyridine-5,5′-diethynyl group.[30,101] The bipyridine moiety in the bridging ligand has been complexed with various metal ions. By this method the luminescence properties of the parent complex can be tuned. Whereas weakly binding ions cause an increase in the luminescence of the Ru(tpy)$_2$-units, strong binders like Ag$^+$ or Hg^{2+} decrease the luminescence. The cause for this behavior is the reducibility of these metal centers, making a photo-induced electron transfer possible which, in turn, results in luminescence quenching. As described in the same publications, the nitrogen atoms have been methylated to lead to a viologen moiety, resulting in a luminescence quenching through electron transfer processes.

In a dyad recently reported by Loiseau,[102] the terpyridine complexes were attached directly to a bridging bipyridine moiety (see Scheme 33). An enhancement of the luminescence was found for protonation of the bipyridine by addition of acids as well as after complexation with zinc(II). Utilizing cyclic voltammetry, it has been found that the electronic interaction between the peripheral chromophores is enhanced by zinc coordination.



Scheme 33 Switchable dyad, containing a bipyridine fragment in the bridging ligand.[102]

A promising approach towards switchable luminescent chromophores are azo-linked ruthenium–osmium dyads.[103] Besides bis-ruthenium and bis-osmium, a mixed ruthenium–osmium dyad has been synthesized (Scheme 34). In these systems, the energy transfer can be switched, triggered by a redox reaction. In its neutral state, the azo-group quenches the luminescence of both the ruthenium and osmium. Reduction of the linker, however, leads to a luminescent homodinuclear Os(II) complex at room temperature.



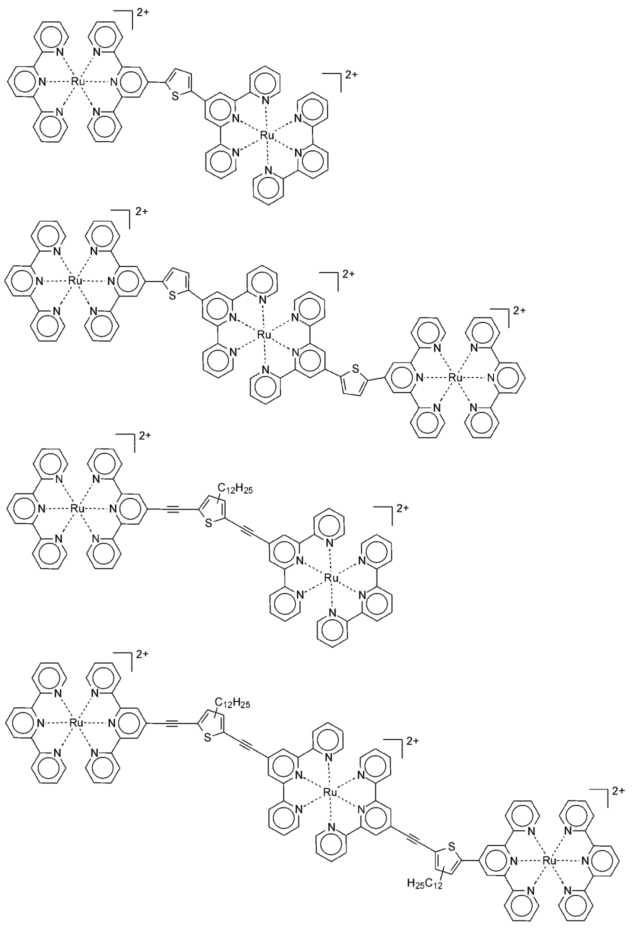
Scheme 34 Luminescence switching by reduction of azo-bridged ruthenium(II)–osmium(II) dyads.[103,104]

The corresponding homodinuclear Ru(II) complex shows a luminescence at 77 K. In the heterodinuclear complex, an energy transfer from ruthenium to osmium can take place, resulting in a strong osmium luminescence (Scheme 34a).

By attaching a coumarin group, the efficiency could be improved further.[104] An energy transfer from the coumarin *via* the ruthenium complex to osmium was observed (Scheme 34b). While the simple Ru–azo–Os dyad revealed an energy transfer of 40%, the coumarin–Ru–azo–Os triad showed an efficiency of more than 70%. Redox-stimulated switching could be performed efficiently.

Besides phenyl and pyridine groups, other aromatic groups have also been introduced into multinuclear complex arrays. A prominent example for a new class of dyads and triads is the "family" of compounds where thiophenes have been introduced (Scheme 35). Besides model complexes (uninuclear complexes bearing one or two thiophenes), dyads and triads with ruthenium ions have been prepared successfully.[105] While the mononuclear complexes already showed an enhanced emission, the multinuclear complexes revealed a luminescence similar to bipyridine–ruthenium(II) complexes. This behavior can be explained by the stabilization of a cluster of luminescent ^{3}MLCT levels in the array by inter-metal electronic communication of the complex units, leading to a higher energy gap and therefore to a lower probability of non-radiative deactivation.

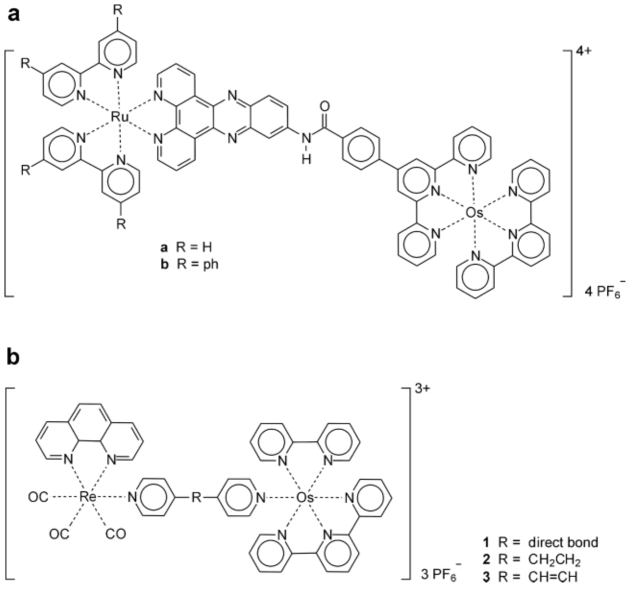
Consequently, this approach has been extended to dyads and triads where the ruthenium complexes have been combined with osmium complexes in order to study energy and electron transfer processes.[106] The mixed complexes are also luminescent, and an energy transfer from ruthenium to osmium could be observed. As a result, luminescence is enhanced when compared to the homometallic complexes. Thus, a five-fold enhancement was found for the Ru–Os–Ru triad.



Scheme 35 Thiophene-bridged dyads and triads.[105]

The well-known chemistry of coupling alkynes to terpyridine has also been applied to couple terpyridine moieties to thiophenes.[107] In this way, systems where the terpyridine and thiophene moieties are separated by an alkyne were obtained. Homometallic ruthenium dyads as well as an ABA-triad (Ru–Zn–Ru) have been prepared. The thiophene unit was found to act as an insulator, preventing full delocalization. An enhanced luminescence was found compared with the uncomplexed mother compounds and compared with the phenylene analogues due to an improved stabilization of the triplet state. The thiophene-linked multinuclear complexes may eventually lead to applications such as molecular wires or as light-harvesting devices.

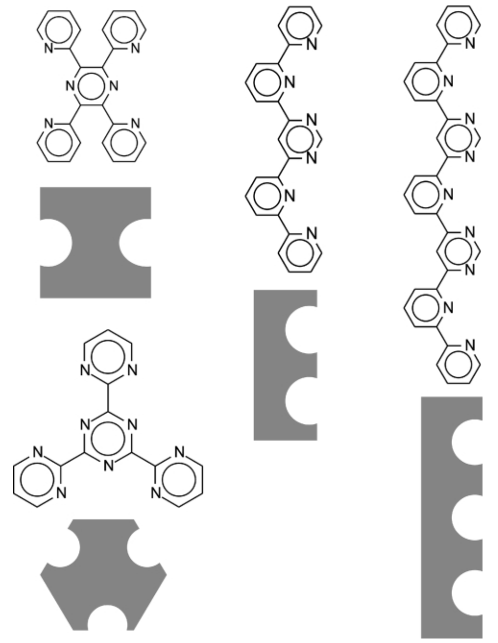
Bipyridine–ruthenium(II) complexes have also been employed in a dyad with terpyridine osmium complexes as a photosensitizer for an enhanced luminescence.[108] This system has been made switchable by the introduction of an aminodipyrido[3,2-a:2′,3′-c]phenazine moiety as a linker (Scheme 36a). The osmium emission could even be increased by the application of 4,4′-diphenyl-2,2′-bipyridine instead of native bipyridine. "Switching" was easily performed through protonation of the connecting unit. The energy transfer system containing an osmium center as a receiving unit has been extended to a "hetero"-system consisting of a pyridine–bipyridine–terpyridine complex (Scheme 36b), to which a rhenium(II) pyridine–phenanthroline–tricarbonyl complex has been connected *via* an ethylene and a vinylene group. An efficient energy transfer was observed in this case.[109]



Scheme 36 Bipyridine–ruthenium–terpyridine osmium dyad, linked by an amide bond (a)[108] and rhenium–carbonyl–osmium dyads (b).[109]

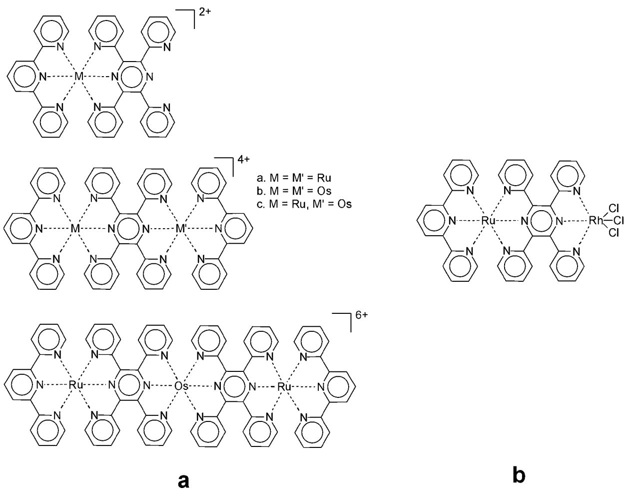
Supramolecular assemblies

So far, oligonuclear complexes were discussed, where two separated terpyridine complexes have been linked together by spacers of various types and lengths. Another possibility for constructing extended complex architectures are ligands where two or more terpyridine motives are combined with sharing one or more nitrogen atoms (Scheme 37). Because the geometry is well defined, these kinds of ligands have been used as building blocks for the construction of extended supramolecular architectures. One example is the ligand tetra-2-pyridyl-1,4-pyrazine (tppz). This molecule can be considered as consisting of two fused terpyridines sharing the central aromatic ring. This allows the construction of rigid rod-like structures (Scheme 38a).[16] Whereas the mono-metallic compounds and the spacer-separated polyads described before show luminescence, the multi-metallic complexes do not emit at room temperature due to metal–metal interaction.



Scheme 37 Building blocks for supramolecular architectures.

Pyrazine ligands have also been used to synthesize mixed Ru(II)/Rh(III) complexes (Scheme 38b).[110] In this case, a mono-metallic tppz-tpy–ruthenium(II) complex has been further complexed with rhodium(III) trichloride. With the rhodium complex known to be an electron acceptor, quenching of luminescence takes place in 80% efficiency *via* an electron transfer.

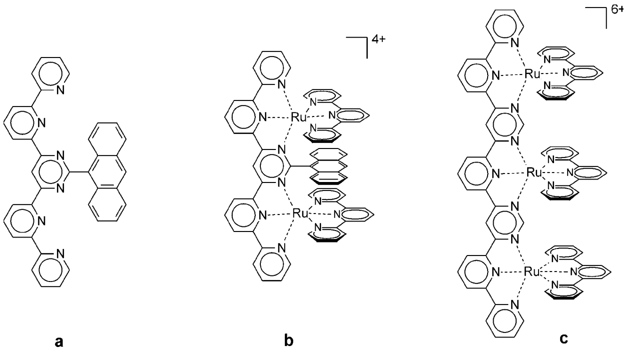


Scheme 38 Complexes of the pyrazine ligand.[16,110]

Grids and racks

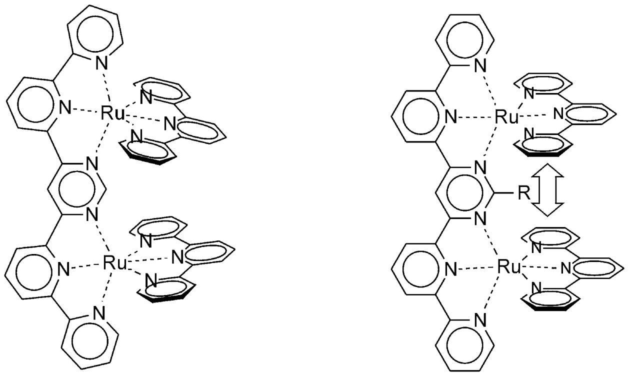
The pyrazine ligand is composed of two fused terpyridines, pointing in 180° directions, allowing the formation of rod-like assemblies. Pyridine rings can also be combined with pyrimidine rings, resulting in ligand systems with fused terpyridine subunits. As opposed to the previously described systems, the coordinating sites are now pointing in the same direction. Two different kinds of assemblies can be obtained from these ligand types, namely grids and racks. In its free, uncomplexed form, the molecule has a helical shape,[111,112] because only this form allows the favored *trans*-conformation of the nitrogen atoms. Therefore, the ligand has to unfold to form complexes.

This type of ligand was first reported by J.-M. Lehn *et al.* in 1995 and was prepared *via* a Stille-type cross-coupling of 6-stannylated bipyridine with 4,6-dichloropyrimidines.[113] Besides a ligand with no further substitution, a molecule bearing an anthryl-substituent in the 5-position of the pyrimidine ring was also synthesized (Scheme 39a). Di- and trinuclear rack-like structures can be achieved by end-capping the terpyridine subunits with the ruthenium(III) mono-complex of unfunctionalized terpyridine (Scheme 39b and c).



Scheme 39 Rack-like complexes.[113]

Crystal structure analysis revealed that the ligand axis is bent due to the not exactly octahedral geometry of the complex unit. This bend is reduced in the case of the anthracene-containing complexes because of the steric repulsion between this moiety and the terpyridine units (Scheme 40). Therefore, the anthryl group is arranged parallel to the neighboring terpyridines. A green color was found for the complexes, which could be explained by the nature of the bridging ligands and metal–metal interactions. UV-VIS spectroscopy showed three MLCT absorption bands due to a splitting of the π*-level. In further work, different substituents such as methyl and phenyl groups, have been introduced into the 5-position of the

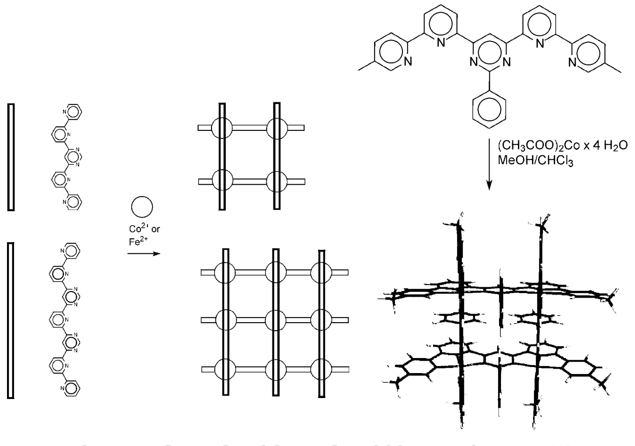


Scheme 40 Distorted geometry of rack-like complexes and their reduction by a bulky substituent in the 5-position of the pyrimidine ring.

pyrimidine, leading to different bending angles of the bridging ligand and convergence angles of the terpyridines, with a methyl group being found to be the best option for a straightened geometry.[114] In the same publication, mono-nuclear complexes where only one site of the bridging ligand is coordinated to a metal ion, were reported. However, the synthesis is more challenging due to activation of the second donor site after metal coordination at the first site.

Photo-physical experiments revealed an emission originating from the anthracene-containing rack-complex in the infrared region.[115] Comparison of the luminescence spectra and lifetimes with the luminescence properties of the subunits showed that in the supramolecular species, excitation energy flows with unitary efficiency to the lowest excited state, regardless of which chromophoric subunit is excited. Luminescence could be observed at room temperature as well as at low temperatures in a rigid matrix and the absorption as well as the luminescence properties could be fine-tuned by changing the substituent at the pyrimidine ring. An energy transfer from the central complexes to the peripheral ones could be observed.[116]

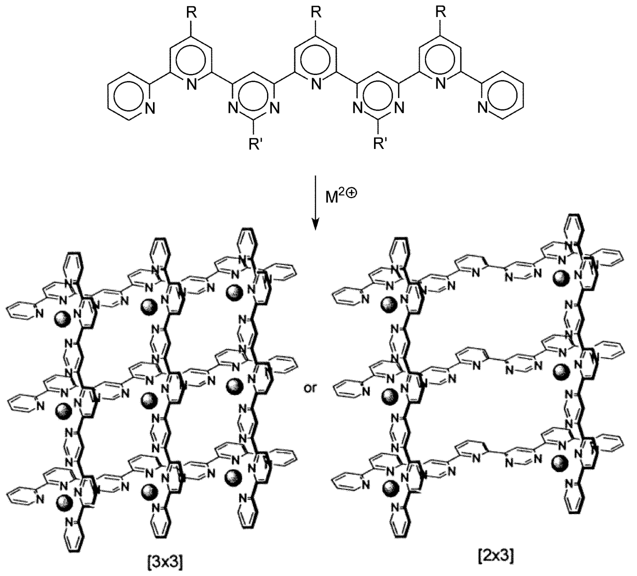
The first examples of grid-like assemblies, based on bipyridine subunits complexed by Ag(I) or Cu(I) ions, were reported in 1992 by Youinou *et al.* ([2 × 2] grids)[117] and in 1994 by the group of J.-M. Lehn ([3 × 3] grids).[118] Most of the work up to now on these architectures has been performed in the laboratories of Lehn and a great deal of research is being carried out today. The principal structure of these complexes is shown in Scheme 41.



Scheme 41 [2 × 2] and [3 × 3] grid-like complexes.[111,112]

The first publications on grids from tris-dentate ligands were published in 1997.[111,112] Through addition of an equimolar amount of hexacoordinating metal ions to the bis-coordinating ligands, analogous coordination arrays are obtained by self-assembly. Supramolecular grids have also been synthesized in the laboratories of Schubert.[119] 4,6-Bis(5″-methyl-2″,2′-bipyrid-6′-yl)-2-phenylpyrimidine was synthesized using a Stille-type coupling in two steps from 2,6-bis(trimethyltin)pyridine (*via* a stannylated bipyridine) and 4,6-dichloro-2-phenylpyrimidine. The product assembled into [2 × 2] grids by the addition of cobalt(II) acetate, and the complex array has been successfully detected in an unfragmented form by MALDI-TOF-MS.[120] The ligand has been prepared in an improved synthesis. The originally described synthesis included a lithiation using butyllithium prior to reaction with trialkyltin chloride, resulting in lower yields, especially when the steps were repeated multiple times. In the new route, sodium stannane was applied, avoiding the lithiation step of the older route and resulting in significantly improved yields. An anti-ferromagnetic spin coupling could be found in the cobalt grid.[121] In the case of iron(II) grids, a spin-crossover from high spin to low spin could be triggered by temperature, pressure and light.[122]

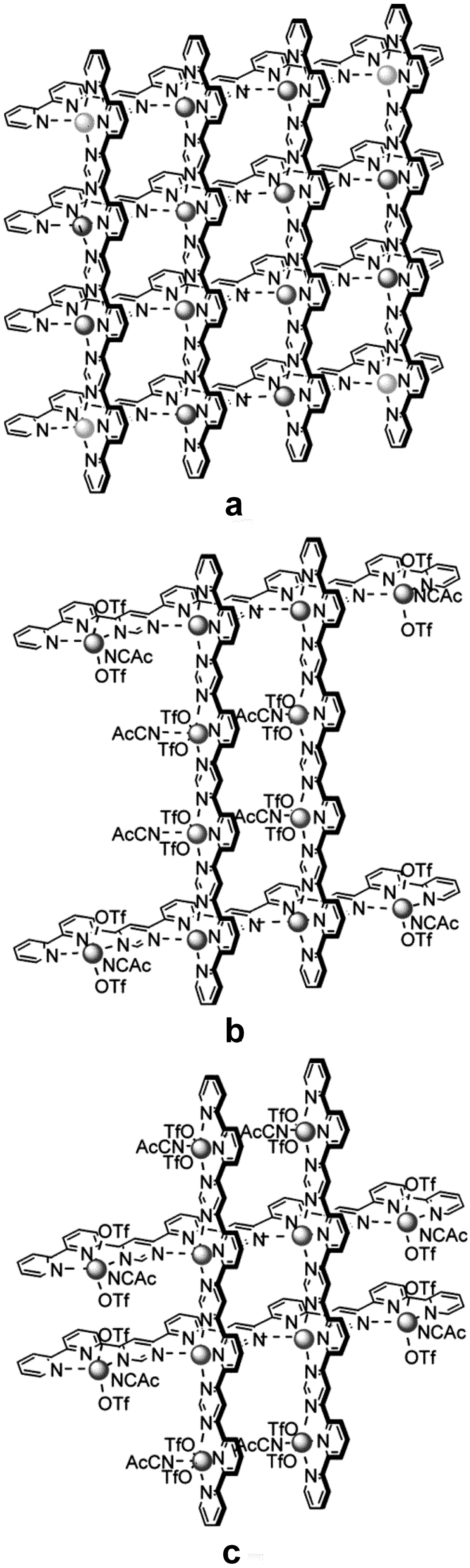
In order to extend the grid-like structures, the synthetic approach was expanded from bis-coordinating to tris-coordinating ligands that are able to form [3 × 3] grids (Scheme 42).[123]



Scheme 42 [3 × 3] and [2 × 3] grids (**a**: R = R′ = H, **b**: R = H, R′ = SnPr, **c**: R = Me, R′ = H, **d**: R = Ph, R′ = H). *Reprinted with permission from* ref. 123 © *2002 Wiley-VCH.*

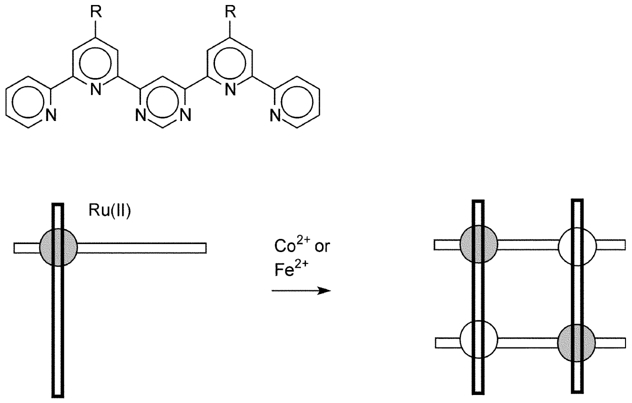
Depending on the used ligands, metal ions and reaction conditions, different grid architectures can be formed. The tris-terdentate ligand composed of three terpyridine subunits that could form either [3 × 3] or incomplete [2 × 3] grids. Whereas zinc(II) tetrafluoroborate with ligand **a** (Scheme 42) and mercury(II) triflate with ligand **b** lead to [3 × 3] structures, the other ligands or other metal ions, such as cobalt, form incomplete grids. Crystal structure analysis revealed the central non-coordinating complex moieties to be in a transoid conformation, which is more stable than the cisoid due to steric hindrance of the ligands and influence from the type of metal ions or counter-ions used. Due to their larger size resulting in less ligand distortion, lead(II) ions were found to be the most suitable metal ions for the assembly of extended grid structures. Using this metal, some very large structures have been reported.[124] A tetra-coordinating ligand has been assembled into [4 × 4] grids by lead(II) ions. By adjusting the stoichiometry, different structures could be obtained, as shown in Scheme 43.[125] A complete [4 × 4] grid was converted into a double-cross shaped structure *via* a double-T shaped [2 × 2] grid structure through the addition of lead triflate to a solution of the ligand. Besides X-ray structure analysis, NMR is a suitable tool for the investigation of such complexes. The structure of the [4 × 4] grid has been determined by ^{207}Pb NMR, which revealed four different metal centers. Moreover, the existence of all types of grids up to the [4 × 4] systems could be shown by electrospray-MS.[126]

Apart from the homometallic grids, which are self-assembled from stoichiometric amounts of ligands and metal ions, attempts have also been undertaken to prepare heterometallic grid structures.



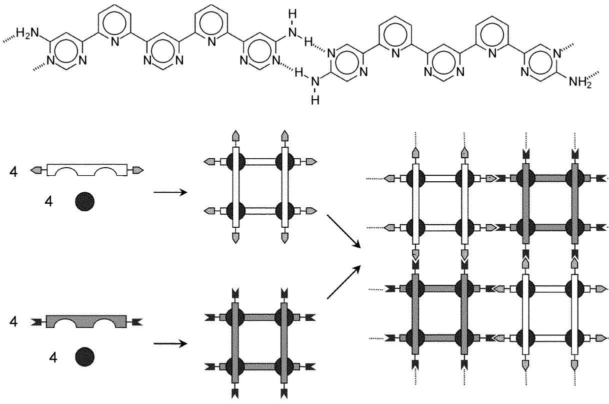
Scheme 43 Grid structures from a tetra-coordinating ligand.[125,126] *Reprinted with permission from* ref. 117 © 2003 *American Chemical Society.*

These reactions need to be performed in a stepwise manner. Initially, one complexation site of the bis-coordinating ligand was converted to a ruthenium(II) complex.[127] Subsequently, iron(II) or cobalt(II) ions were added to this intermediate (which is chiral), resulting in self-assembly to a grid-like complex (Scheme 44).



Scheme 44 Heterometallic grid complex.[127]

In an extension of the self-assembly principle, two-level self-organization can be achieved by the use of two different ligands that bear complementary hydrogen bonding units at the periphery (Scheme 45).[128] These compounds were converted to the grid-like complexes, respectively. Mixing stoichiometric amounts of each complex resulted in a highly organized "grid of grids".

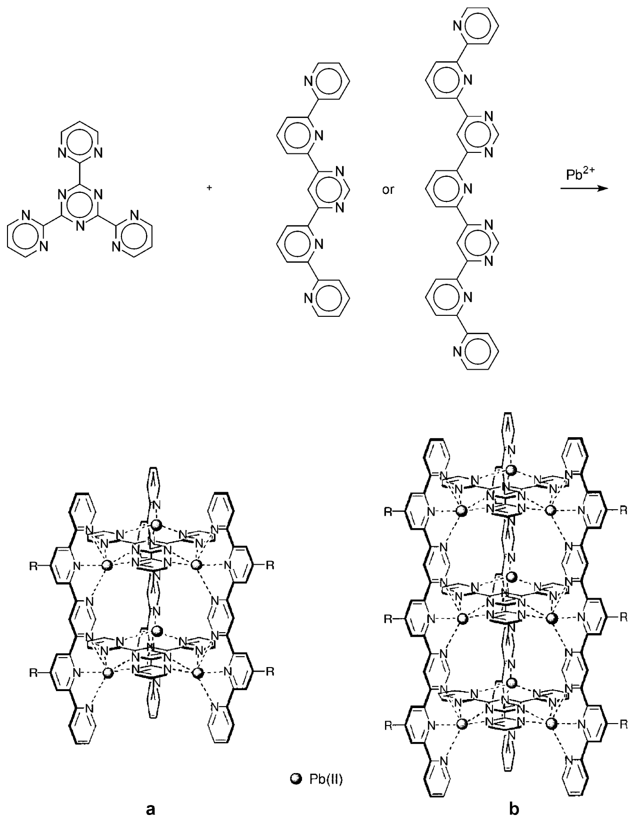


Scheme 45 Two-step self-assembly to a "hypergrid" by hydrogen bonding.[128]

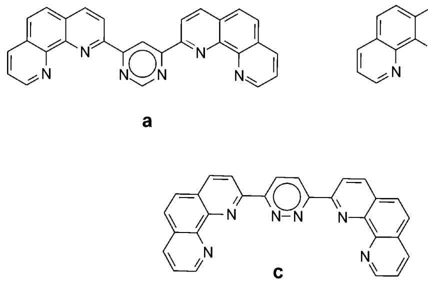
Complexes composed of different metal centers could be assembled in this fashion, giving rise to chessboard like layers. Another approach consisted of the introduction of pyridine rings in the 4′-position of the terpyridine subunits.[129] The free ligand as well as the resulting grid-complexes could be assembled on graphite surfaces. Weak CH–N hydrogen bonding interactions were also postulated by the authors, based on STM observations and comparisons with molecular modelling results.

Besides racks and grids, other architectures are also conceivable. When adding lead(II) ions to a mixture of tris-2,4,6-(2-pyrimidyl)-1,3,5-triazine and bridged ligands consisting of two or three fused terpyridine moieties, self-assembly took place, resulting in cylindrical cage-like complexes, constructed of either 6 or 9 metal centers, respectively (Scheme 46).[130] In this case, 36 respective 54 coordination bonds between 11 respective 15 components are formed in one reaction step, demonstrating the power and selectiveness of the self-assembly reaction.

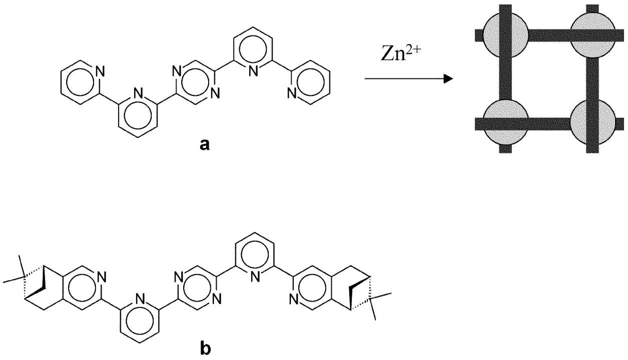
The concept of multiple chelators has been continued by the synthesis of phenanthrolinyl-based systems.[131] Bis-tridentate ligands of the "Lehn-type" as well as molecules where the chelating moieties are pointing in 180° directions have been prepared (Scheme 47). All the corresponding mono- and dimetallic Ru(II)–terpyridine complexes could be prepared, only in the case of the



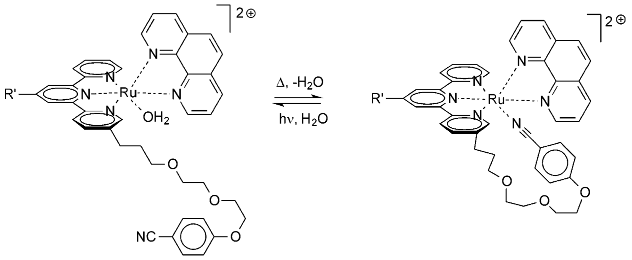
Scheme 46 Cylindrical complex array. *Reprinted with permission from* ref. 130 © *1999 Wiley-VCH.*



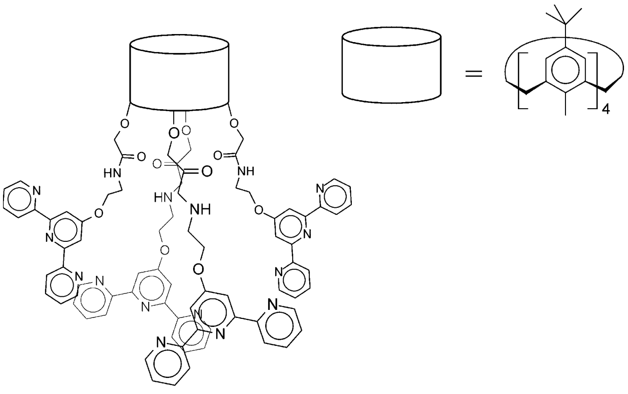
Scheme 47 Phenanthroline-based bis-coordinating ligands.[131]



Scheme 48 Formation of chiral “grid”-like assemblies.[132]



Scheme 49 Scorpionate terpyridine complex.[133]



Scheme 50 Calixarene–tetraterpyridine.[134]

pincer-shaped ligand **c**, the dinuclear complex was not accessible because of steric hindrance.

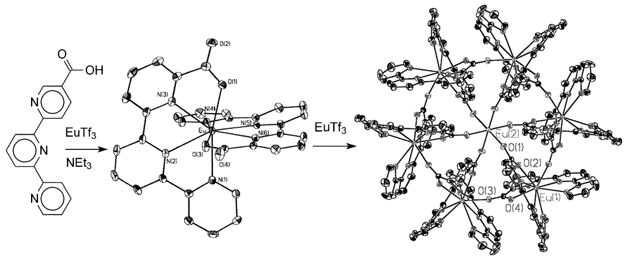
Ligands of the structure as shown in Scheme 47b are able to form supramolecular assemblies consisting of four ligands and four metal ions. Unlike the “Lehn-type” grids, these structures possess a D_4 symmetry and are therefore chiral.[132] Whereas the unsubstituted ligand Scheme 48a) forms a racemic mixture of the supramolecular compound, the self-assembly could be directed in a stereoselective fashion by attaching pinene groups onto the terminal pyridine rings (Scheme 48b).

Other assemblies

A novel switchable ruthenium complex is represented by the “scorpionate” system depicted in Scheme 49.[133] A Ru(II) complex was synthesized from a 1,10-phenanthroline unit and a terpyridine ligand, linked to a benzonitrile. The latter, in turn, is able to coordinate to the ruthenium metal center, in a “back-biting” manner. The coordinated benzonitrile group can be reversibly replaced by water either through thermal or photochemical induction (Scheme 49).

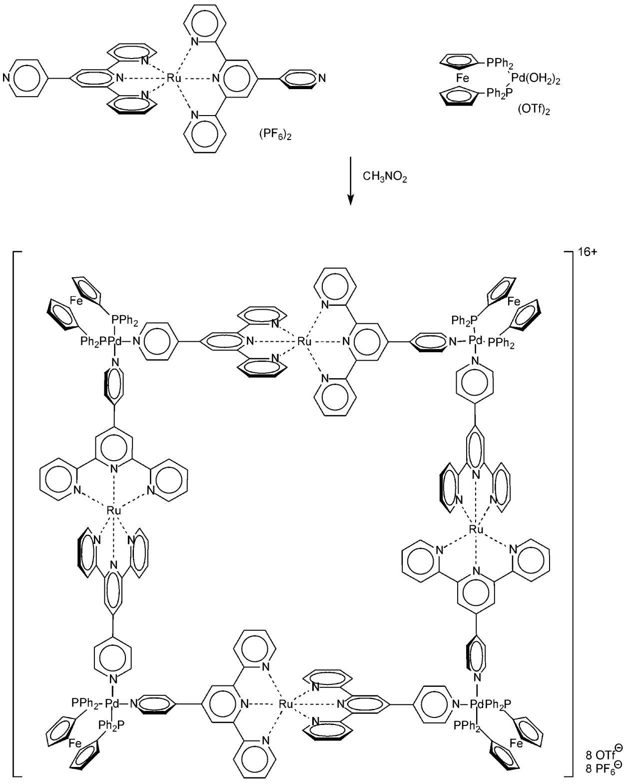
A calix[4]arene that has been modified with four terpyridine moieties can be prepared to act as a scaffold-like “pre-organizer” for supramolecular architectures (Scheme 50).[134] Complexation with nickel(II), copper(II) and cobalt(II) led to the formation of intramolecular complexes incorporating two metal ions.

A wheel-like self-assembled structure has been achieved using 6-carboxy terpyridine, which acts as a tetradentate ligand.[135] At a 2 : 1 ratio of the ligand to europium triflate, a mononuclear bis-complex was formed. Addition of more europium ions resulted in self-assembly to the hexanuclear complex of a wheel-like structure, where the carboxylates act as bridging ligands between the subunits. An octahedrally coordinated seventh europium ion lies in the center, coordinating to all six complex units (Scheme 51).



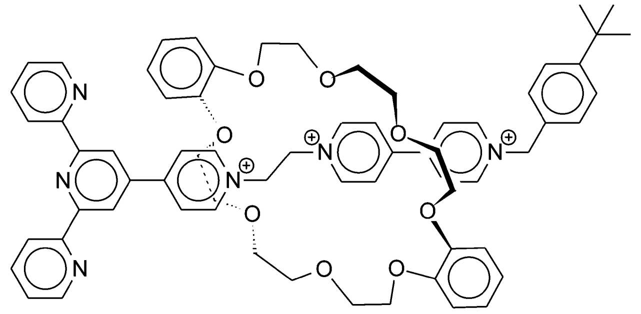
Scheme 51 Wheel-like europium–terpyridine complex. *Reprinted with permission from* ref. 135 © 2002 *American Chemical Society.*

Large molecular squares have been obtained, which contained platinum or rhenium complexes in the corners and terpyridine complexes as bridging ligands (Scheme 52).[136,137] Pyridyl–terpyridine complexes of iron, ruthenium and osmium have been employed in a self-assembly reaction with $BrRe(CO)_5$ or $(dppf)Pd(H_2O)_2(OTf)_2$ (with dppf = 1,1′-bis(diphenylphosphino)-ferrocene). These complexes act as corner-points and possess a square-planar coordination geometry, therefore leading to square-shaped structures. Multi-electron redox processes were observed in the assemblies, and luminescence was detected for the osmium-containing compound but not for the others.



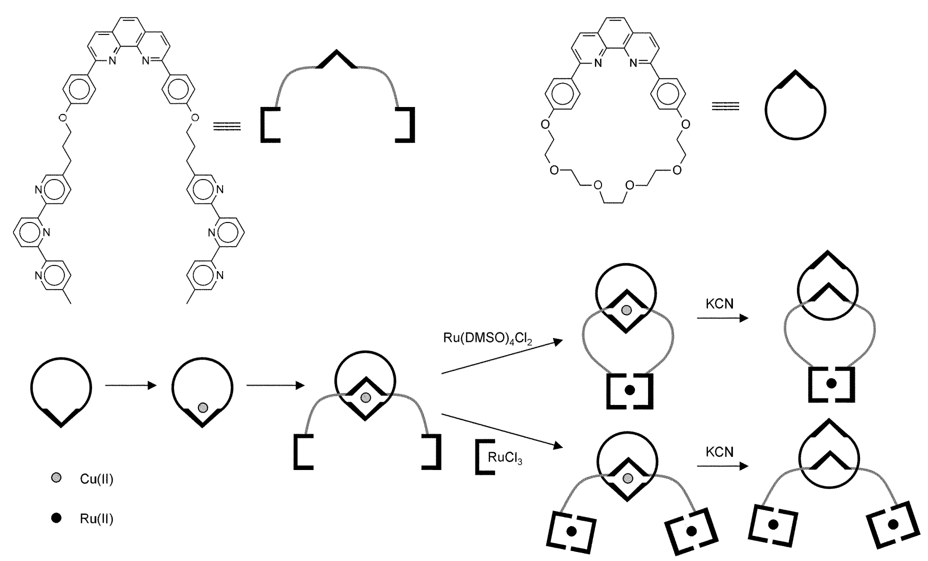
Scheme 52 Multi-metallic supramolecular squares.[136,137]

Rotaxanes of 4′-functionalized terpyridine were presented in a recent publication:[138] A cationic (dipyridinium)ethane system acts as an axle in a supramolecular system with crown ethers, which has been locked by end-capping the axle with a bulky end-group after the self-assembly process (Scheme 53). Unsubstituted 24-crown-8 as well as the dibenzo- and dinaphthyl-analogues have been employed. Iron(II) complexes of all ligands have been prepared, showing a significant red-shift of the metal–ligand charge transfer absorption band for the complexes containing the crown ethers with the aromatic substituents. The crystal structure of the ligand revealed a π-interaction of the substituent of the crown ether with the terpyridine unit. This interaction causes a stabilization of the MLCT in the complex. Another example from the same group opens the way to rotaxanes as well as catenanes (Scheme 54). A 2,9-bis(phenyl)phenanthroline that was incorporated into a crown ether ring structure was first converted into a copper(II)-mono-complex (bis-complexes are not possible due to steric hindrance). The subsequently added terpyridine–phenanthroline–terpyridine strand threads into the ring to form a bis-phenanthroline–copper(II) complex. Afterwards the terpyridine ends were locked with terpyridine–ruthenium(III) fragments to yield the rotaxane, or closed with $Ru(DMSO)_4Cl_2$, resulting in the catenane. In a final step, the copper ion can be removed by addition of KCN to lead to the free rotaxane respective catenane.[139] The catenane was re-metallated with zinc(II) and silver(I) ions. Photo-physical investigations of all systems revealed electron and energy transfer processes in the compounds with the direction being dependant of the metal ion used. Whereas the ligand centered luminescence is quenched in the case of zinc(II), silver(I) and the free catenane, the opposite effect takes place for the copper(II) catenane. Therefore, this system could be of interest as a potential "molecular switch".[140]

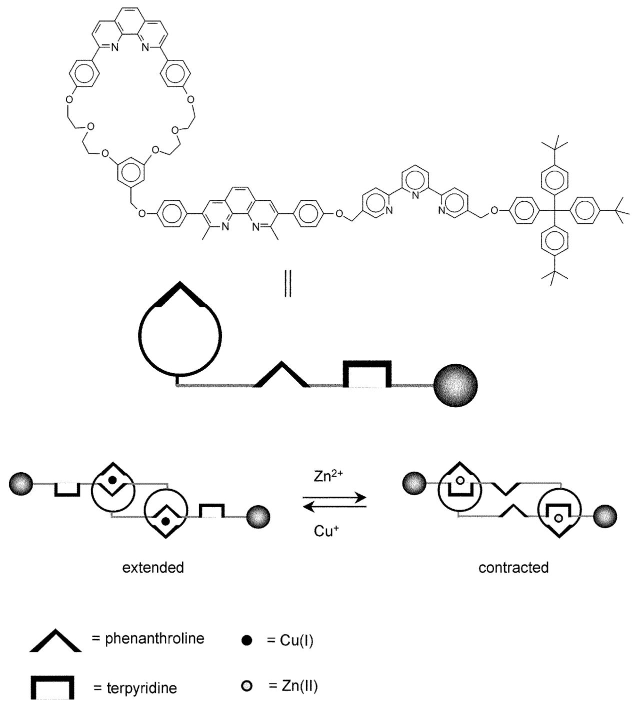


Scheme 53 Schematic representation of a terpyridine, consisting of a rotaxane assembly with a crown ether.[138]

An extended molecule consisting of a phenanthroline moiety within a crown ether-like ring structure, connected to another phenanthroline bound to a terpyridine moiety (bearing a bulky endgroup in the 5″-position) in the 5-position has been prepared and subsequently self-assembled with copper(I) ions to form a linked bis-rotaxane.[141] After exchanging the metal ion to zinc, the coordination switched from a tetra-coordinated to a penta-coordinated system, involving the terpyridine moiety (Scheme 55). The resulting reversible extension and contraction represents a first



Scheme 54 Rotaxanes and catenanes *via* the self-assembly of tetrahedral phenanthroline followed by the formation of ruthenium(II)–terpyridine complexes.[139,140]



Scheme 55 "Molecular muscle" by redox-switchable terpyridine–phenanthroline complexes.[141,142]

step towards novel applications such as artificial muscles or molecular machines. For an article focussing on molecular muscles see ref. 142.

Cycles

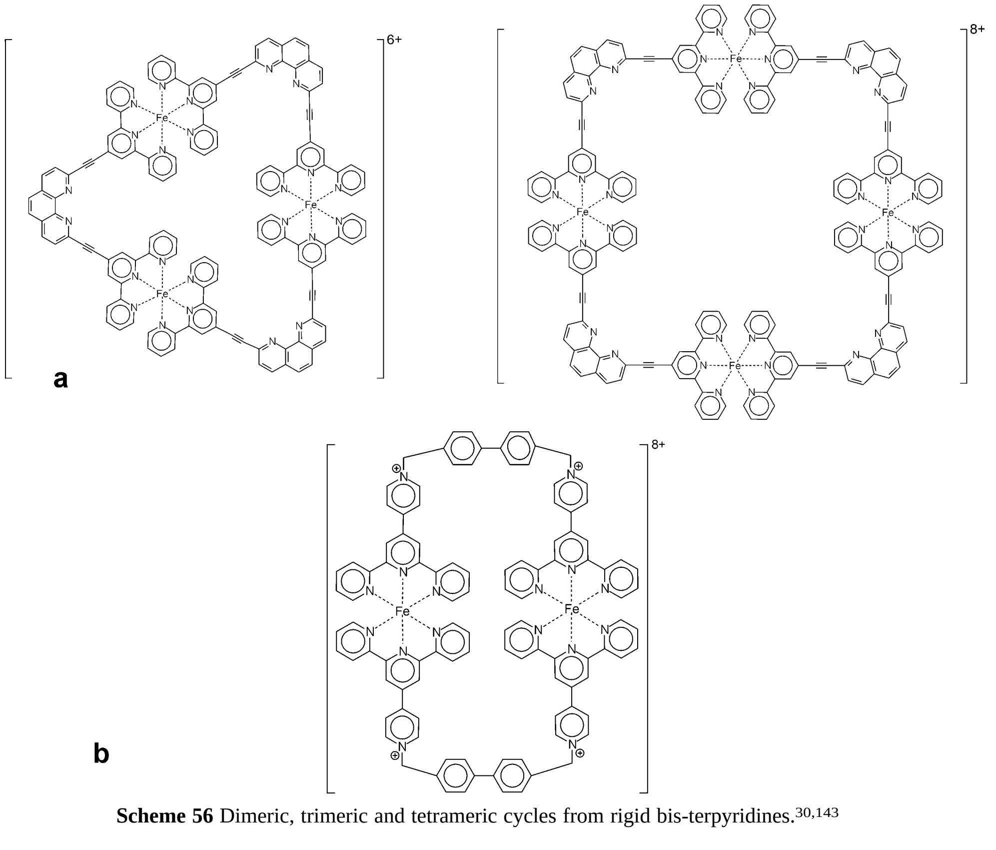
Bis-terpyridines with suitable spacers are able to form ring structures by complexation with metal ions. Cycles based on rigid bis-terpyridines were the first reported examples. Whereas linear rigid systems form polymers, groups with an angle in the spacer group result in cyclic complexes. Due to the given geometry, the size of the rings is predetermined. Synthetically easily accessible linkers are the rigid ethynyl group, reviewed by Ziessel (Scheme 56a).[30] The 60° angle of the two ethynyl–terpyridines, connected to the phenanthroline, favor a tricyclic structure, but also the less stable tetra-cyclic analogue was formed.

In another example, the synthesis of box-like cycles has been reported.[143] The bis-terpyridine ligand was obtained by alkylation of the pyridyl-*N*-atom of 4′-(4-pyridyl) terpyridine with 4,4′-bis(bromomethyl)biphenyl. Complexation with iron(II) ions yielded a bicyclic compound as the main product (Scheme 56b).

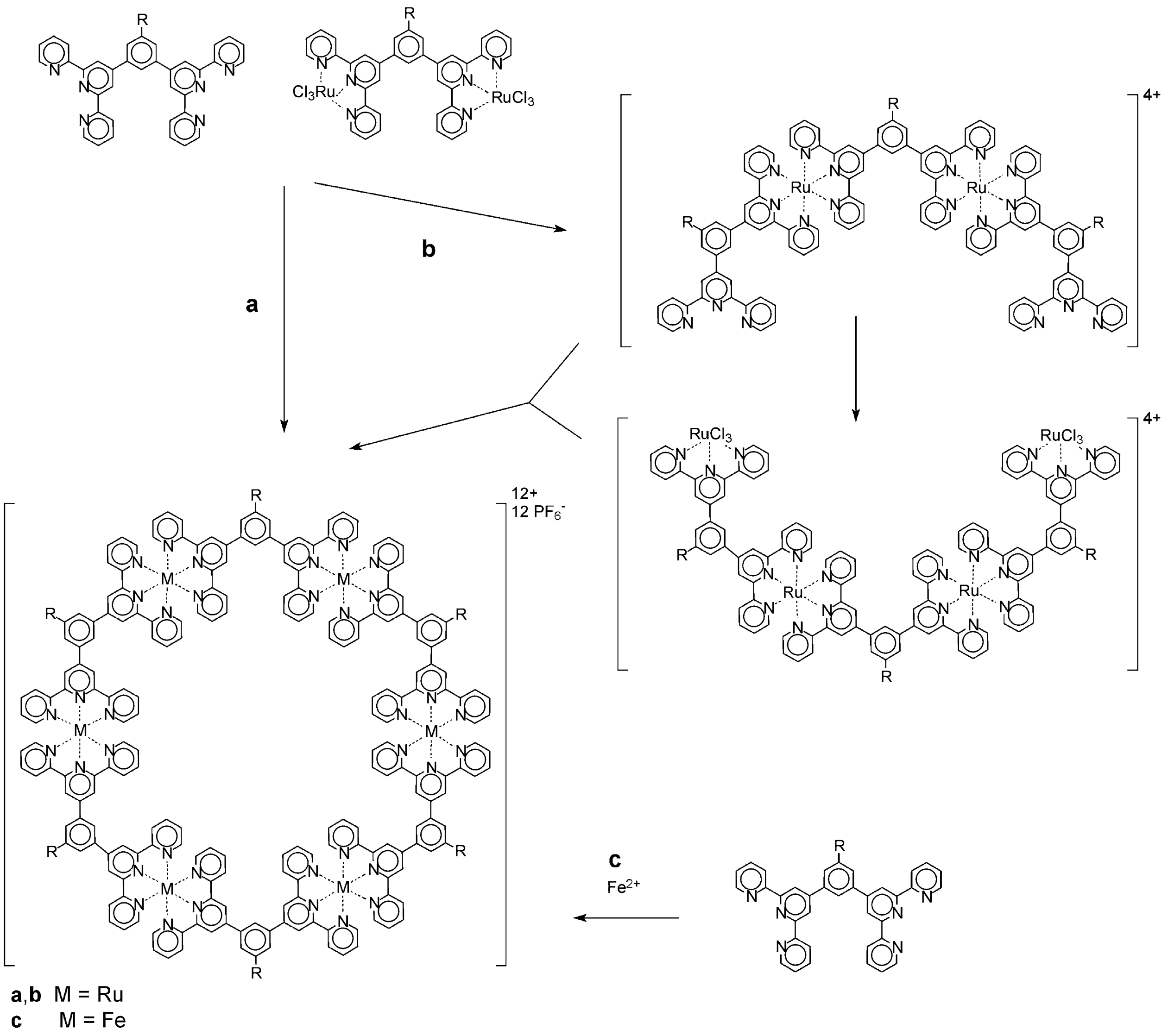
An interesting cycle was presented by Newkome *et al*.[144] A *meta*-bis-terpyridyl phenyl ring was complexed with iron and ruthenium, leading to a hexameric cycle. This geometry is favored due to the 120° angle present in the ligand. Two approaches were used to obtain the ruthenium cycle (Scheme 57). In a self-assembly by reacting stoichiometric amounts of free ligand and of the ruthenium(III) mono-complex of the ligand (route a), the product was obtained. In the second approach (b), the macrocycle was constructed by a stepwise reaction *via* "half-rings" as the intermediate. Moreover, an analogous cycle was prepared by adding iron(II) ions to the ligand, leading to exclusive formation of the hexameric cycle. Beside standard techniques and cyclic voltammetry, the existence of the macrocycles was also proven by TEM.

So far, most cycles were constructed from building blocks consisting of a rigid spacer, in which the direction of complexation is predetermined by the angle within the spacer group. Therefore, cycles were obtained exclusively in well-defined sizes.

The formation of cyclic products from bis-terpyridines linked by flexible spacers is much more challenging, because these telechelics allow the formation of different sized rings as well as polymeric compounds. Despite these difficulties, different flexible groups have been employed in the synthesis of rings. Due to the flexibility, a mixture of various rings and coordination polymers were obtained in most cases. Therefore, low concentrations had to



Scheme 56 Dimeric, trimeric and tetrameric cycles from rigid bis-terpyridines.[30,143]



Scheme 57 Hexameric cycle by Newkome *et al.*[144]

be applied in order to push the ring-chain equilibrium to the side of ring formation. Furthermore, purification of the product by column chromatography mixture is necessary.

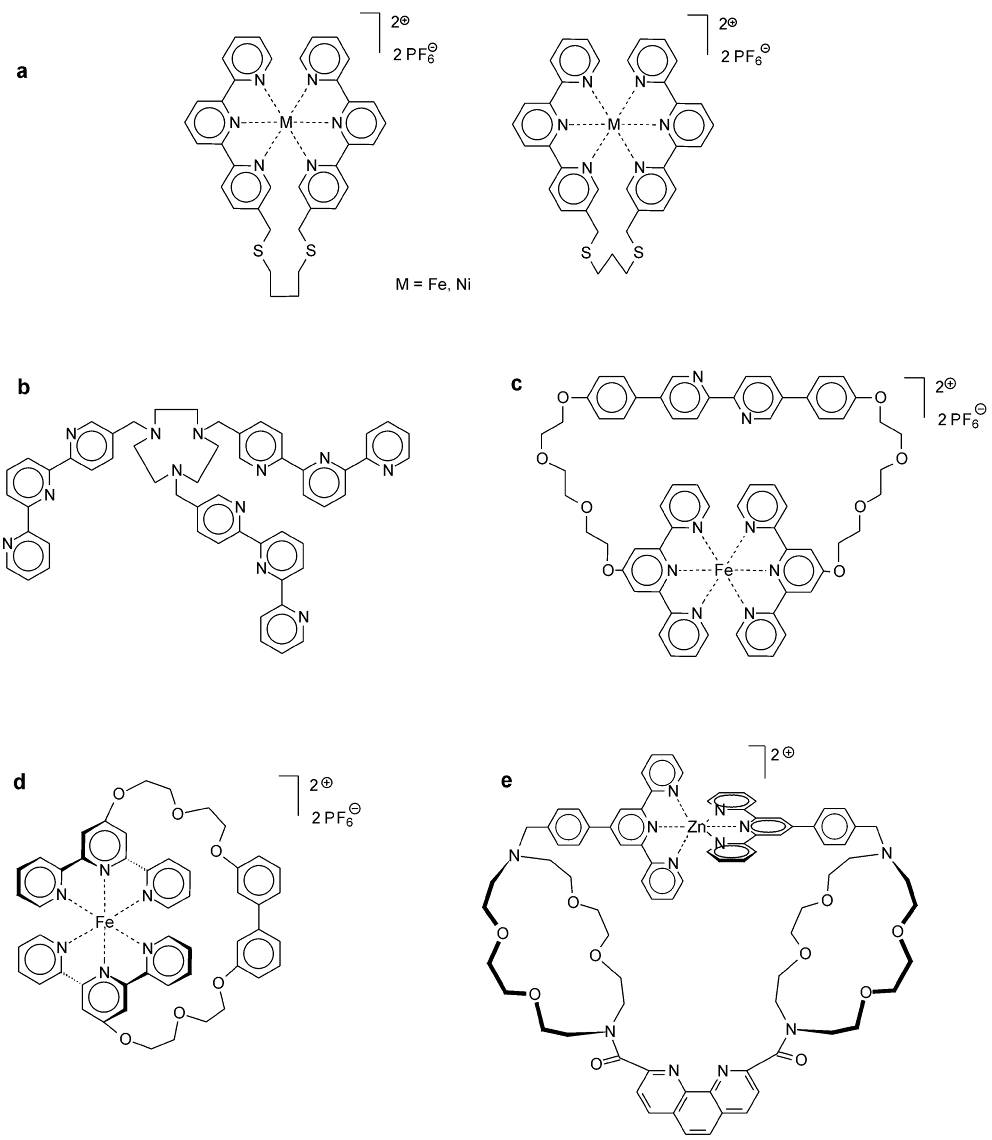
Mono-cycles can only be formed if the spacer possesses sufficient flexibility and an appropriate length. In the following example from the group of Moore, the terpyridines are linked in the 5-position by a 1,3-bis(2,2′:6′,2″-terpyridyl-5-ylmethylsulfanyl)-propane and a 1,4-bis(2,2′:6′,2″-terpyridyl-5-ylmethylsulfanyl)-butane spacer, both of which are 7 or 8 atoms long.[145] This length was predicted to be optimal by molecular modelling. The addition of Fe(II) or Ni(II) ions resulted in an intramolecular cyclization, which was verified by X-ray structure analysis (Scheme 58a). When adding the free ligand to a solution of an iron(II) complex of unfunctionalized terpyridine, a ligand exchange was observed, leading to the cyclic complex. This behavior can be explained by the chelate effect. In the same manner, three terpyridine moieties could be connected to a cyclic triamine (Scheme 58b).[146] Complexation of this ligand to europium(III) led to a room temperature luminescent bicyclic complex involving all terpyridine groups.

In all of these cases, the terpyridines are connected in the 5-position. Due to this fact, the connecting points of the resulting complex are in close proximity, therefore even short spacers allow successful complexation.

4′-Functionalized terpyridines, where the functionalities are on the opposite faces of the complex, require much longer spacers or a special geometry. The system shown in Scheme 58c, where the terpyridine moieties are linked *via* tri(ethylene glycol) spacers to a rigid 5,5′-bisphenyl–bipyridine domain, has been synthesized by the group of Constable.[147] Flexible chains are protruding in 120° angles from the rod-like central unit, thus the terpyridine groups are able to embrace the metal ions, allowing the formation of mono-cycles. This was confirmed by X-ray crystal structure analysis. The bipyridine unit is accessible for further complexation in order to construct extended supramolecular systems. In continuing experiments, a mono-cycle containing a 2,7-(diethylene glycol)naphthalene linker, has been prepared (Scheme 58d). The “handle” is conformationally locked in the cleft between the terpyridine moieties, resulting in a chiral structure.[148]

Another unimolecular ring structure was obtained from a multifunctional ligand (Scheme 58e). An extended polytopic ligand, containing two terpyridine moieties that were linked *via* crown ether moieties to a central phenanthroline unit, was complexed to Zn(II) ions to form a mono-cyclic complex.[149] In a different experiment, the terpyridine end-groups were complexed to bipyridine–ruthenium(II) fragments.

A recent result reported by Constable *et al.* describes the synthesis of cycles of different sizes.[150] The terpyridines were linked by flexible triethylene glycol chains in the 4′-position. This geometry does not allow the formation of mono-cycles because the linker is too short. Therefore tris- and tetra-cycles were obtained as well as some polymeric material (Scheme 59). To



Scheme 58 Mono-cycles of 5- and 4′-linked bis-terpyridines.[145–149]

minimize the amount of polymeric product, the concentration was kept low (0.4 M), and the products were isolated by column chromatography. The composition of the products was analyzed by ESI-MS, furthermore a shift of the ^{1}H NMR signals of the terpyridine protons compared to the polymer was found, which was attributed to the different chemical environments of the aromatic protons in the rings. Similar cycles, in this case with hexyl-spacers linking the terpyridine moieties, have been prepared recently.[151] A tris- and a tetra-cycle could be isolated and identified by MALDI-TOF mass spectrometry.

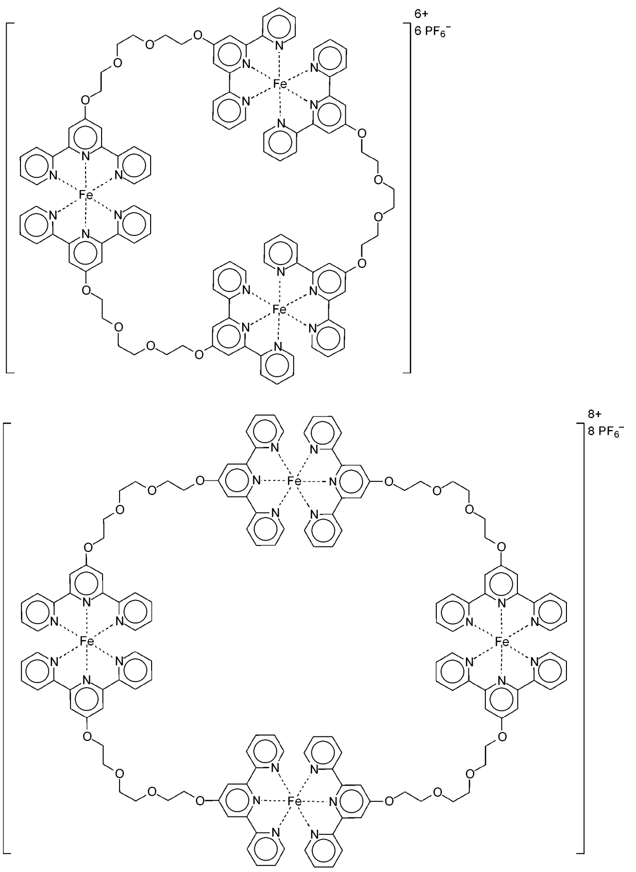
The first examples of metallodendritic spiranes (spirometallodendrimers) were obtained in the group of Newkome[152] *via* incorporation of four terpyridine units within each dendritic quadrant of dendrimers with a pentaerythrol core (Scheme 60). These moieties were subsequently complexed to iron(II) and ruthenium(II) ions, leading to intramolecular cyclization of the spiro type.

An interesting cyclic architecture has been reported recently:[153] two different macorocycles (each containing two terpyridine moieties, with the coordination site facing *endo* in the one and *exo* in the other) were threaded by the formation of ruthenium(II) complexes (Scheme 61). Crystal structure analysis revealed an orthogonal arrangement of the two cycles. This supramolecular architecture represents the first step towards the molecular "Borromean link" of three orthogonal rings (interweaving of three rings to form an integral molecular unit without catenation of two cycles).

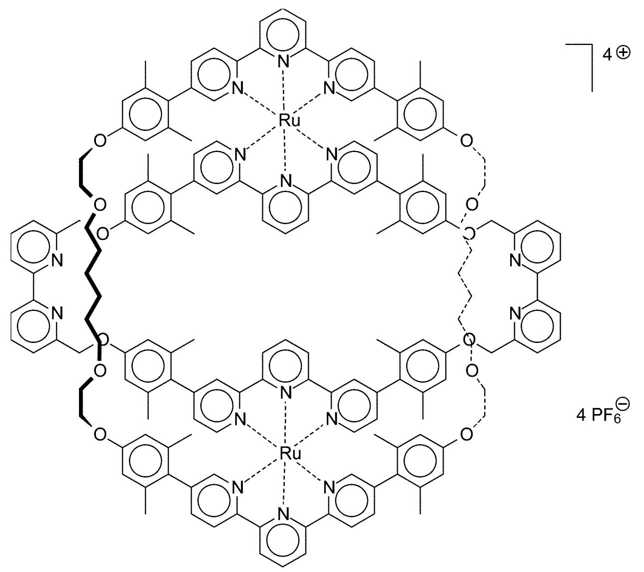
Fullerene terpyridine complexes

Fullerenes are of special interest in contemporary chemistry due to their photo-physical and electrochemical properties, which make them interesting in the context of the development of novel molecular electronics or light harvesting devices and may eventually lead to potential applications such as organic solar cells. Most of the current research into these particular kinds of solar cells includes fullerenes due to their electron-accepting properties.

One approach has been the combination of fullerenes with terpyridine–ruthenium(II) complexes. The pioneering work in the field was performed by the group of Constable and Diederich *et al.*[154,155] Terpyridines, bearing a malonate ester group linked by oligo(ethylene glycols) were prepared in two-step reactions (Scheme 62). A Bingel reaction of brominated malonates with C_{60} (loss of the bromine and addition to an unsaturated fullerene bond) led to fullereno–terpyridines. In another reaction, the terpyridine was directly attached to the fullerene by adding a brominated terpyridinyl acetic acid ethyl ester under Bingel conditions to C_{60}. The functional ligands were subsequently converted to the corresponding Ru(II) complexes by ruthenium(III)/(II) chemistry. In the case of the compound where the units are spatially close, a



Scheme 59 Flexible oligo-cycles by Constable.[150]

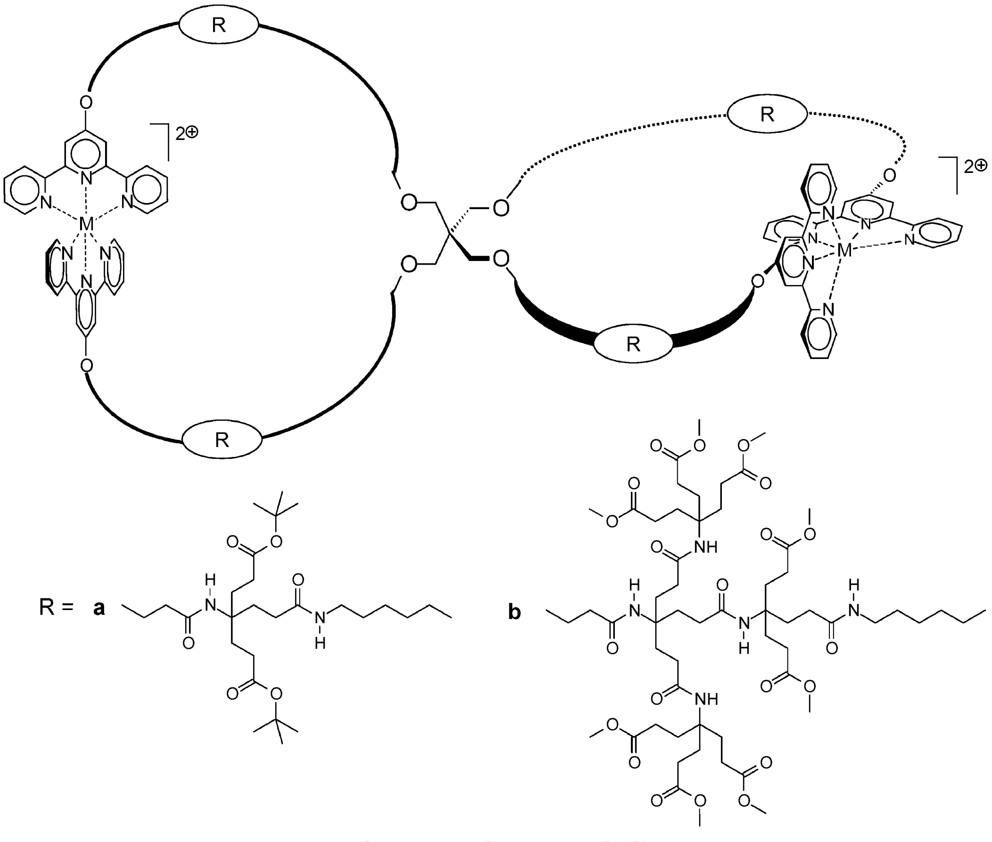


Scheme 61 Construction of a "Borromean link".[153]

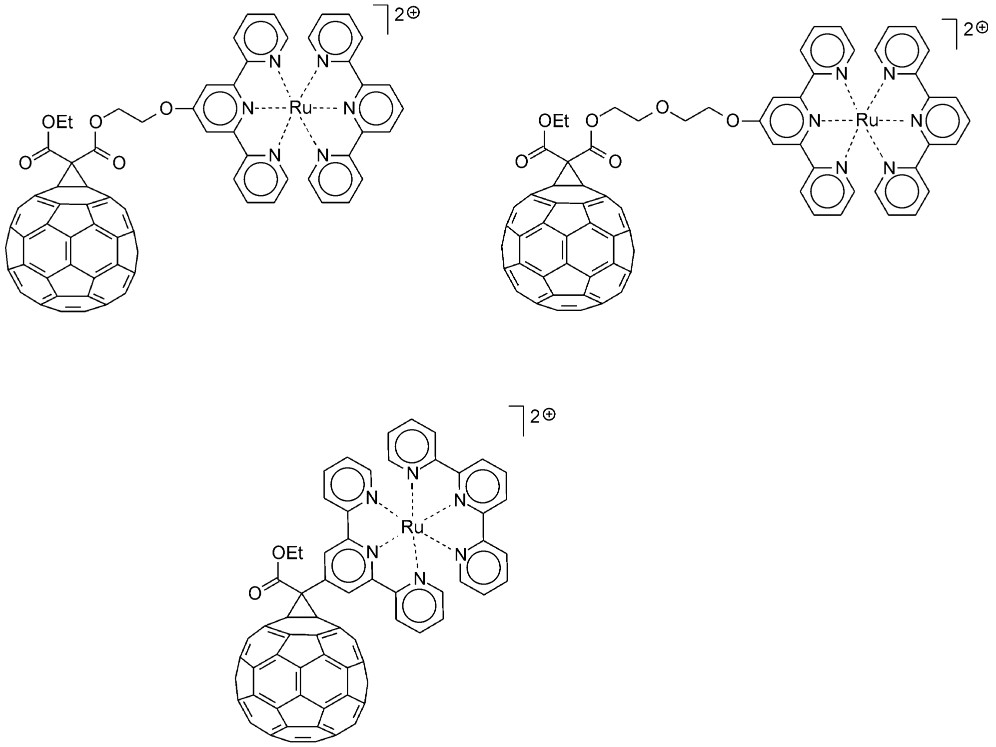
strong interaction between the fullerene and the terpyridine complex was found by cyclic voltammetry.

The approach was continued in the group of Schubert.[156] A functionalized fullerene (obtained in several steps including a Diels–Alder reaction) that contains an acid chloride has been reacted with an aminoterpyridine, resulting in a terpyridinyl–fullerene, linked by an alkyl group. AB dyads and ABA triads were prepared by complexing the ligand to a terpyridine–Ru(III) mono-complex or a second equivalent of the functional ligand and $RuCl_3$ (Scheme 63a–b).

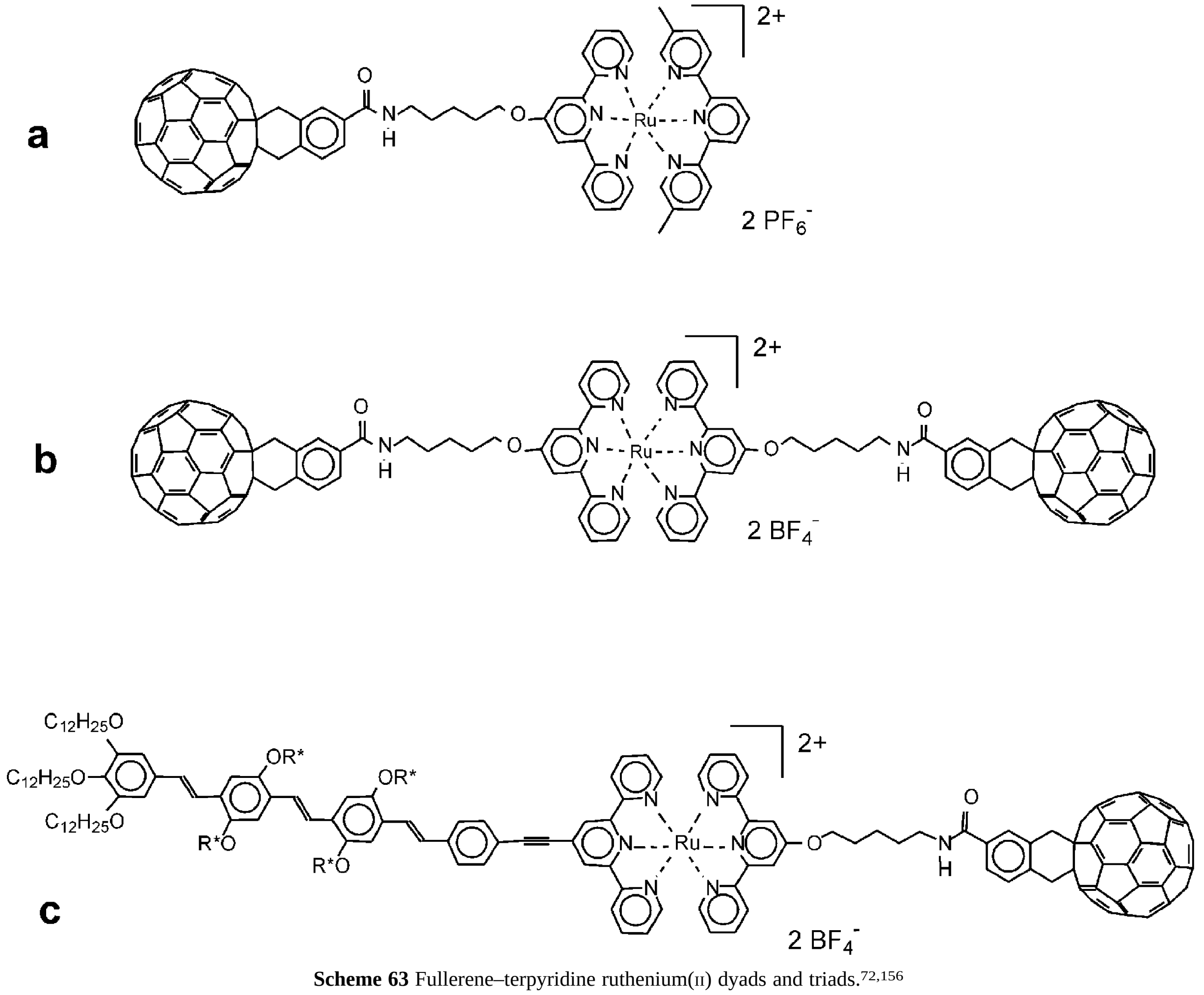
Another molecular moiety that has been studied intensively in the context of organic solar cells, is the highly luminescent and electron-donating oligo(*p*-phenylene vinylene) (OPV), that has already been covalently linked to fullerenes. Recently, the combination of these two units has been achieved *via* the formation of a terpyridine–ruthenium(II) complex, leading to an ABC triad (Scheme 63c).[72] Photo-induced absorption experiments revealed a lifetime of the charge-separated state of less than 100 μs (this is the timescale of the experiment, thus the actual lifetime could not be



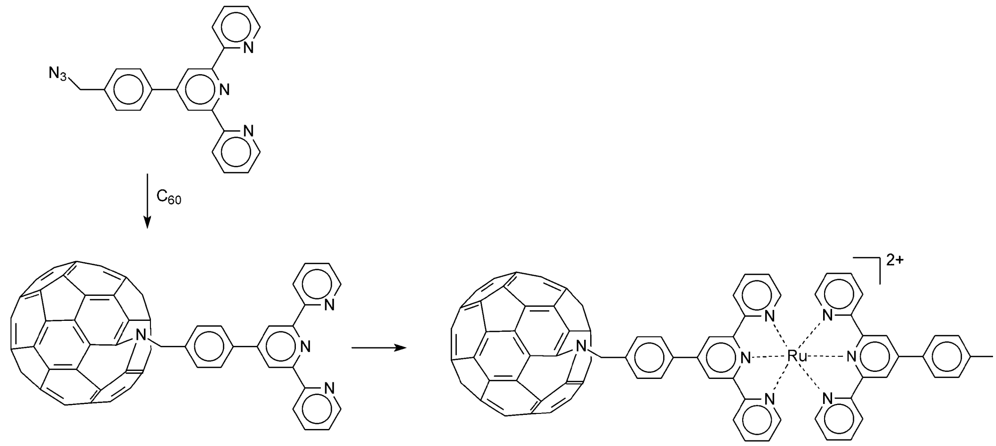
Scheme 60 Dendritic spirocycle.[152]



Scheme 62 Fullerenes, containing terpyridine complexes, linked by spacers of various length.[154,155]



Scheme 63 Fullerene–terpyridine ruthenium(II) dyads and triads.[72,156]



Scheme 64 Coupling of an azide-functionalized terpyridine to a fullerene.[157]

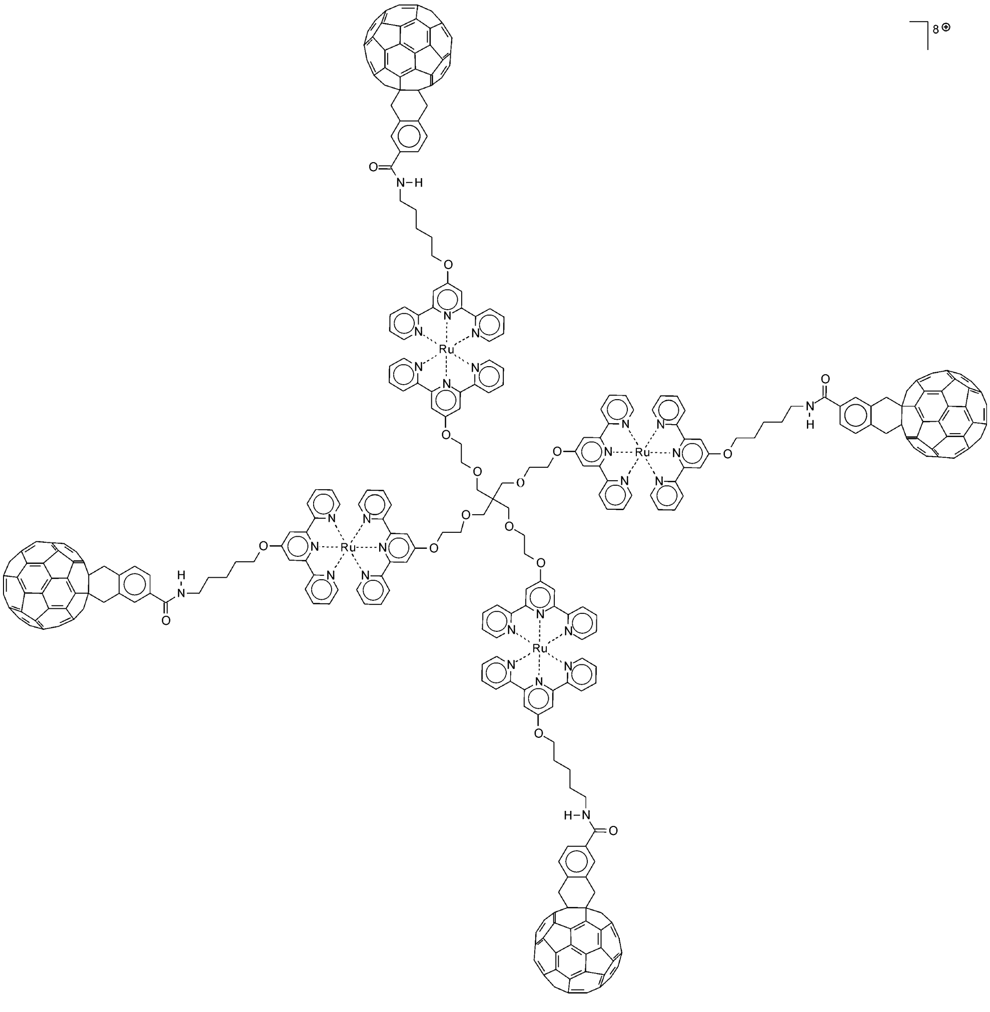
determined). Energy transfer from the OPV to the fullerene resulted in the quenching of the OPV luminescence.

In the group of Li, tolyl–terpyridine has been converted to an azide.[157] The cycloaddition reaction of this intermediate to the fullerene resulted in a ring-opening of the fullerene cage (1.6-aza-bridged, Scheme 64). Subsequent complexation with tolyl–terpyridine–ruthenium led to the fullerene–ruthenium complex dyad.

In the group of Schubert, even a tetra-fullerene adduct was successfully prepared. A tetra-terpyridine, based on pentaerythrol, was reacted with a terpyridine-containing fullerene derivative (Scheme 65). The result is a star-shaped complex with buckyballs in the periphery.[158]

Complexes containing biochemical groups

An interesting approach is the combination of terpyridine-complex chromophores with biomolecules, which could act as luminescent labels for biological processes. Furthermore, the ability of electron

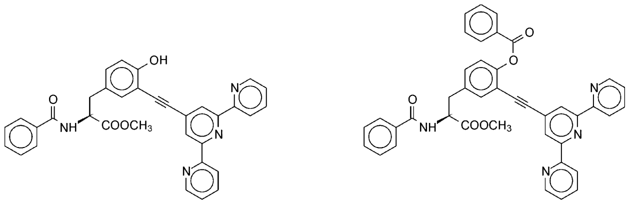


Scheme 65 Star-shaped tetrafullerene complex array.[158]

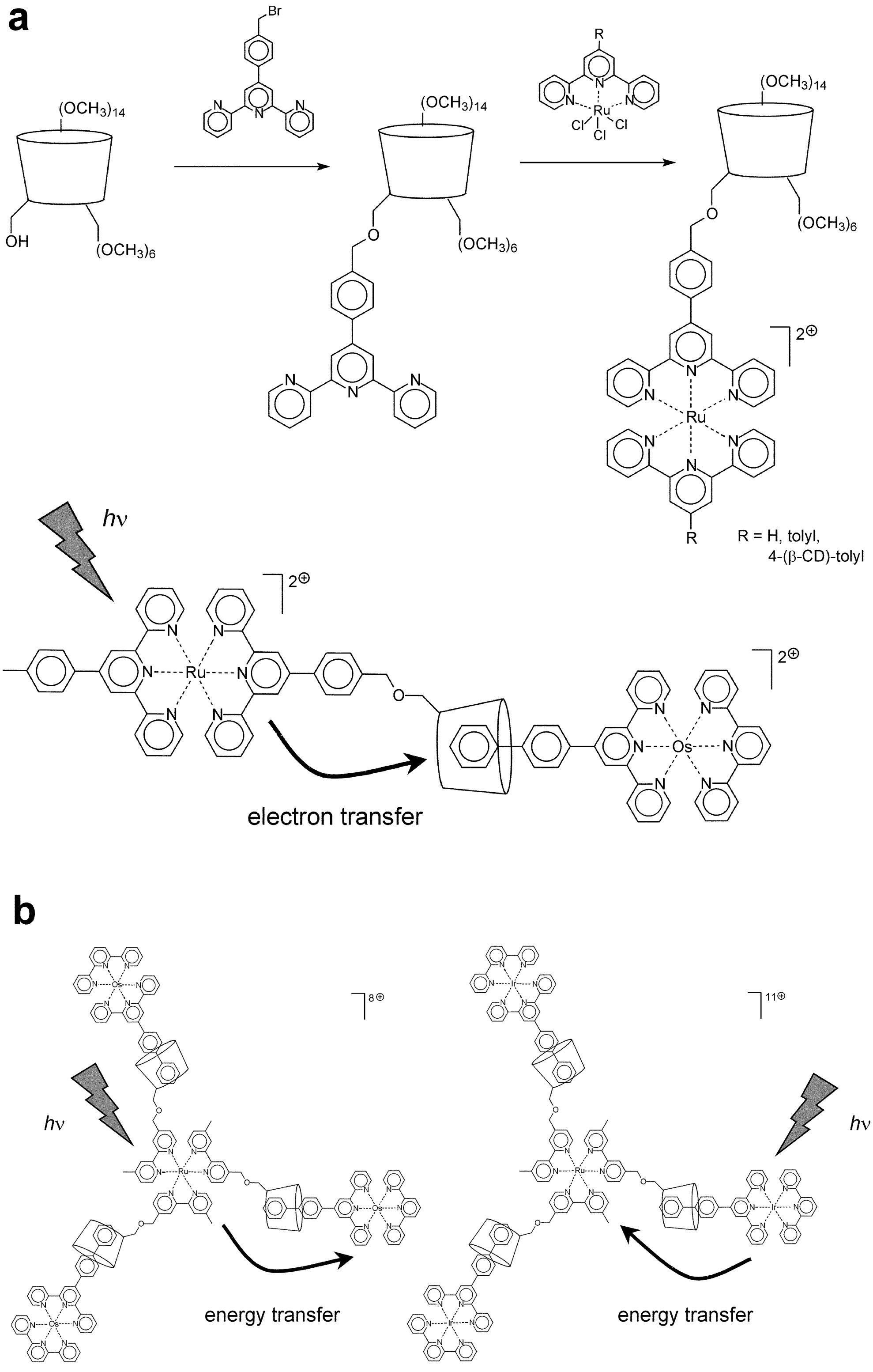
transfer could help to study electron transfer processes in biological systems.

Ziessel *et al.* reported the synthesis of a terpyridine, containing an L-tyrosine group (Scheme 66) and the subsequent formation of the corresponding ruthenium(II) complexes.[159] This combination was chosen for future studies of "Photosystem II" (where water is oxidized to oxygen), a large membrane bounded protein system. It could also help to construct artificial water oxidation catalysts.

An ethynyl group was chosen as linker and the palladium-catalyzed coupling of the iodide of the tyrosine group with the 4′-



Scheme 66 Terpyridine, bearing an L-tyrosine group.[159]



Scheme 67 (a) Cyclodextrin-functionalized terpyridine complexes and binding of a metallo-guest[160,161] and (b) binding of terpyridine complexes of osmium(II) and iridium(III) to a cyclodextrin-functionalized bipyridine–ruthenium(II) complex, enabling energy transfer processes.[162]

triflyl(terpyridine). Besides a compound containing a free phenolic group, a complex bearing a protected group was prepared.

While a solution of the unprotected complex in acetonitrile shows luminescence even at room temperature, it is quenched in a K_2CO_3-containing DMF solution, indicating an electron transfer from the phenolic group of the tyrosine moiety in basic conditions by photoexcitation, followed by back-electron transfer. In the protected compound, the phenol is blocked, therefore no electron transfer is possible and as a result, emission was observed.

Cyclodextrin cups were employed to build supramolecular systems, consisting of a 4′-tolylterpyridine ruthenium complex and a guest-binding moiety (Scheme 67a).[160] All but one of the methyl groups of the cyclodextrin were protected before attachment of the terpyridine fragment (4′-*p*-(bromomethyl)phenyl-terpyridine) by a Williamson type ether coupling.

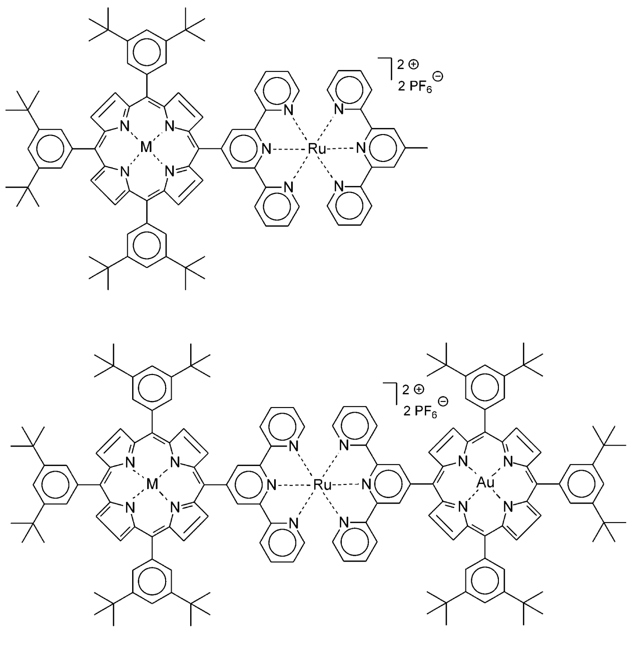
This functional ligand was subsequently complexed with terpyridine–ruthenium(III) trichloride and 4′-*p*-tolyl(terpyridine)–ruthenium(III) trichloride, respectively, with the latter known to be room temperature emitting. The final product may act as an optical sensor for the hydrophobic binding of guests to the cyclodextrin, as shown for the addition of anthraquinone-2-carboxylic acid. A quenching of the phosphorescence was observed, caused by an intermolecular electron transfer from the ruthenium complex to the quinone.

In further studies (also including a bis(cyclodextrin) complex), different quinone guests were used, leading to a luminescence quenching of different intensities, depending on the kind of quinone.[161] In another experiment, a biphenylterpyridine–terpyridine–osmium(II) complex (biphenyl group as a guest) was added to the host system. In the resulting Ru–Os system, an electron transfer from ruthenium to osmium could be observed after oxidation of the osmium center. However, a Ru(II)–Os(II) energy transfer was not detected due to the short lifetime of the ruthenium emission (in accordance with covalent dyads, linked by saturated spacers). This energy transfer could be achieved by the use of long-lifetime complexes.[162] In the present case, a ruthenium(II) complex of three bipyridines bearing cyclodextrins was synthesized (Scheme 67b). The binding of terpyridine metal complexes, containing a guest-binding unit (biphenyl or adamantyl) resulted in an energy transfer. Moreover, the direction of the energy transfer could be reversed, depending on the metal center of the guest-complex; whereas osmium(II) complexes lead to an energy transfer from ruthenium to osmium (core to periphery), the direction is reverted by iridium(III) complexes as guests. The energy transfer from the three peripheral complexes to the ruthenium core makes such systems interesting as light harvesting devices.

The novelty of this host–guest system, compared to the ones previously described (dyads), is that both donor and acceptor are being brought together spatially *via* non-covalent interactions.

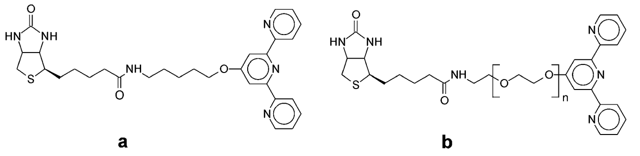
A variety of porphyrin–ruthenium complex conjugates, AB dyads, ABA and ABC triads were constructed and investigated by Flamigni *et al.*, the ruthenium-based component being a strong electron and energy acceptor.[163–166] The porphyrin site has been studied when both uncomplexed as well as complexed to either zinc(II) or gold(II) ions (Scheme 68). A photo-induced two-step electron and energy transfer could be observed. The singlet excited state porphyrin is first quenched by the ruthenium component, leading to a ruthenium complex localized triplet excited state (^{3}MLCT) which, in turn, transfers its triplet energy back to the porphyrin unit attached to it so as to generate the porphyrin triplet excited state. The same authors also utilized terpyridine–iridium(III) complexes for the porphyrin triad system, showing a multi-step electron transfer from the free or zinc(II)-complexed porphyrin *via* the iridium complex to the gold(III)-complexed porphyrin.[48,167]

Another approach in combining biochemistry with terpyridine supramolecular chemistry is the coupling of biotin to a 4′-aminoterpyridine, applying the well-known isocyanate coupling reaction.[168] Besides a short alkyl-spacer, a polymeric poly(ethylene glycol) chain has also been introduced (Scheme 69). Biotin is known to bind strongly to the protein avidine *via* multiple hydrogen bonding, with a geometry comparable to a "lock and key" system.



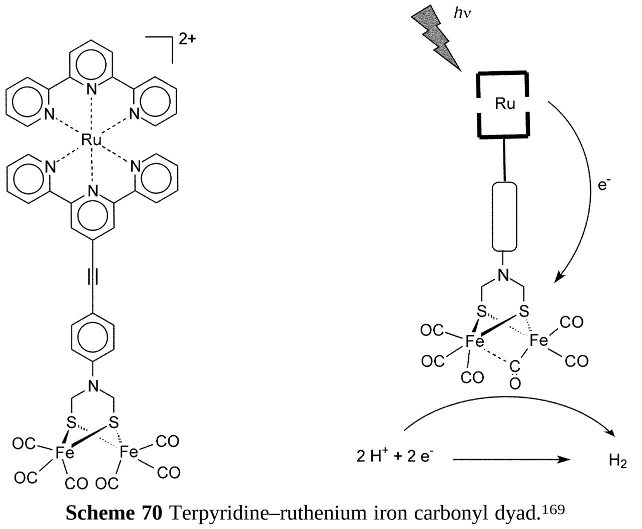
a M = Zn
b M = 2 H

Scheme 68 Porphyrin–terpyridine complexes.[163–167]



Scheme 69 Biotin-functionalized terpyridine ligands.[168]

In a recent publication, a dinuclear iron carbonyl complex was attached to a terpyridine–ruthenium complex, mimicking the active site of iron–hydrogenase (Scheme 70).[169] Irradiation of the complex resulted in an electron transfer, which could be utilized to produce hydrogen.



Scheme 70 Terpyridine–ruthenium iron carbonyl dyad.[169]

Another recent contribution describes the connection of DNA fragments to terpyridine complexes.[170] Two complementary DNA sequences (20 base pairs) were connected *via* tri(ethylene glycol) to a terpyridine moiety, respectively, and subsequently the corresponding symmetric ruthenium(II) complexes were prepared. The mixing of these two complexes resulted in long linear arrays through self-assembly, where the length could be adjusted by the molar ratios of the ligands in the mixture.

Conclusion and outlook

In conclusion, terpyridine is one of the most suitable ligands for the construction of supramolecular systems through metal coordination due to the relatively strong and directed metal bonding. Extended architectures can be obtained by directed reaction as well as self-assembly. Among the advantages of such complexes is the reversibility, which makes the terpyridine-containing compounds interesting in materials research and for the introduction into polymers. Finally, the electronic and optical properties, especially of ruthenium(II) and osmium(II), are of importance for potential applications such as solar cells and nano-devices because they allow the exploitation of the “light-harvesting properties” of the complexes through energy and electron transfer processes as well as through their inherent switchability. Further work will focus on the improvement of the systems and attempts to introduce the products into actual applications.

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