Probing the effect of coordination environment on the photophysical behavior of rhenium(I) luminophores

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Joensuu 2019
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To be presented with the permission of the Faculty of Science and Forestry of the University of Eastern Finland for public criticism in Auditorium N100, Yliopistokatu 7, Joensuu, on May 16th at 12 noon.

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ISBN: 978-952-61-3079-8
ISSN: 2242-1033

Grano Oy  
Jyväskylä 2019
ABSTRACT

The development of versatile light-emitting compounds and materials is crucial in various technological fields including optoelectronic devices, photodynamic therapy, sensing, photocatalysis, bio-imaging, and high-performance solar cells. As a result, a large number of luminescent dyes were created over the years. Much of the research to date has focused on transition metal complexes, due to the variety of their molecular configurations that allows significant freedom in molecular design to attain unique photophysical characteristics. Among the transition and rare earth metal photofunctional compounds, the rhenium(I) luminophores have remarkable stability, low toxicity, and appealing physical properties. Thus, they have attracted ever-increasing interest from both academic and industrial researchers.

This work explores the synthetic approaches to new rhenium(I)-based luminescent compounds with enriched photophysical behavior. Taking the archetypal emitter [Re(CO)₃(NN)Cl] (NN = diimine) as a starting point, I attempted to alter the optical characteristics through two approaches: (i) modification of the coordination sphere of Re(I) center by means of the diimine and auxiliary ligands, and (ii) introduction of secondary chromophore units to the parent rhenium motif.

The first strategy, meant to improve the photophysical properties, is based on incorporation of the peripheral ancillary ligands into the {Re(CO)₂(NN)} core, which bears a common chelating diimine (NN = phenanthroline). A series of alkynylphosphines served as auxiliary axial ligands with different donor ability and stereochemistry, which were accessibly modulated by changing the number and length of alkynyl-phenylene substituents.

The second route of structural modification aims at extending the range of luminescence colors to the whole visible spectrum. Such wide color-tuning of [Re(CO)₃(NN)Cl] emissions was achieved by integrating secondary chromophore moieties into the pyridyl-phenanthroimidazole ligand.

Another feasible way to manipulate the photophysical behavior relies on the construction of homo- and heterometallic rhenium-containing coordination assemblies through merging two or more metal chromophores. The utilization of flexible connecting bridges diminishes the communication between the constituting components, while noncovalent intermolecular interactions substantially diversify the optical properties of the bimetallic assemblies. On the other hand, coordination-driven self-assembly using rigid cyanide linkers illustrates a facile way to attain supramolecular aggregates decorated with multiple {Re(CO)₃(NN)} chromophores.

Results from the present project should contribute to a more comprehensive understanding of the structure-property relationships for the family of rhenium(I) chromophores. This, in turn, should assist in elaborating novel molecular systems with advanced photophysical functionality.
LIST OF ORIGINAL PUBLICATIONS

This dissertation is a summary of original publications I–IV.


Author’s contribution

The research material for the listed publications was obtained by the author and the collaborating groups, who performed theoretical, magnetic and electrochemical investigations. The author was responsible for the synthesis of all the compounds in publications I-IV (except compounds L9, 7, 9, 11 in publication I). The author carried out NMR, IR and structural characterization of all novel compounds. The author also carried out the photophysical measurements for all the complexes discussed in the thesis. The author participated in analyzing the computational results and in writing the original publications.
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ACKNOWLEDGEMENTS
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ABBREVIATIONS

CIE coordinates  Chromaticity coordinates
D-A   Donor-acceptor
DFT   Density functional theory
DMF   Dimethylformamide
DMSO  Dimethyl sulfoxide
dppz   Dipyridophenazine
dpyb   Dipyridinebenzene
EL    Electroluminescence
ESI-MS Electrospray ionization mass spectrometry
HOMO  Highest occupied molecular orbital
ILCT  Intraligand charge transfer
IR    Infrared
ISC   Intersystem crossing
LC    Ligand-centered
LLCT  Ligand-to-ligand charge transfer
LUMO  Lowest unoccupied molecular orbital
MLCT  Metal-to-ligand charge transfer
NMR   Nuclear magnetic resonance
OLED  Organic light emitting diode
PhotoCORM Photo-activated carbon monoxide releasing molecule
PNI   4-(1-Piperidinyl)naphthalene-1,8-dicarboximide
ppy   2-Phenylpyridine
S\(_0\)  Singlet ground state
SOC   Spin-orbit coupling
T\(_1\)  Lowest triplet excited state
TD-DFT Time-dependent density functional theory
THF   Tetrahydrofuran
UV/vis Ultraviolet/visible
XRD   X-ray diffraction
1 INTRODUCTION

The chemistry of rhenium began in 1925, when the vacant slot below manganese in the periodic table was filled by Walter Noddack, Ida Tacke and Otto Berg, who were the first to isolate this new element from the mineral gadolinite. Occupying the slot below manganese in the periodic table, rhenium was the last-discovered element that has a stable isotope, namely $^{185}\text{Re}$ with a cosmic abundance of 37.07%. Meanwhile, $^{187}\text{Re}$ (mole fraction: 62.93%) is radioactive with a half-life of 41 billion years. Rhenium is among the least abundant elements both in the Earth’s crust and in the solar system. Natural sources that have a relatively high Re content for its economic extraction as the primary commodity are extremely scarce. Currently, Re is commercially obtained as a by-product in the process of molybdenum refining.

Although rhenium is the congener of manganese, these two elements have very different chemical properties due to the phenomenon of secondary (supplementary) periodicity. An important chemical characteristic of rhenium is the presence of several oxidation states that can readily interconvert under mild conditions. The lower oxidation states (1, 0, and -1) are typically found in a large number of carbonyl derivatives and related organometallic compounds, which is similar to the family of manganese relatives.4

The first coordination compounds of rhenium were discovered in the 1930s. In 1939, Walter Hieber and colleagues reported the synthetic route to the distorted octahedral rhenium(I) complexes $\text{[Re(CO)₅Hal]}$ by treating the corresponding hexahalogenorhenate(IV) with carbon monoxide.5 This work laid the foundation of a successful research direction for rhenium(I) carbonyl compounds. In 1958, G. Wilkinson described the substitution reactions that convert $\text{[Re(CO)₃I]}$ into the di-pyridine derivative $\text{fac-[Re(CO)₃(py)₂I]}$.6 Further, R. Pietropaolo confirmed the preferential $\text{fac}$-configuration of the rhenium(I) tricarbonyl compounds (Figure 1) by IR spectroscopic measurements, and rationalized the result by analysis of the $\pi$ backdonation between the rhenium atom and the carbonyl ligands.7

Figure 1. $\text{fac}$-Configuration of the complex $\text{[Re(CO)₃(py)₂I]}$.6

In the 1970s, Wrighton and coworkers prepared the tricarbonyl diimine rhenium(I) complexes $\text{[Re(NN)(CO)₃L]}$ (L = axial ligand) and performed the first systematic study
of their photophysical behaviors. As a result, they discovered a diverse class of Re-based organometallic luminescent materials.

1.1 Modulation of the photophysical behavior of rhenium(I) luminophores through variation of the ligand environment

Upon photoexcitation, most rhenium(I) carbonyl diimine complexes can undergo several types of electronic transitions, such as ligand-centered\(^9\),\(^10\) (LC) transitions, metal-to-ligand,\(^8\),\(^11\),\(^12\) intraligand,\(^13\),\(^14\) and ligand-to-ligand\(^15\),\(^16\) charge transfers (MLCT, ILCT, and LLCT, respectively).\(^17\)

The intense high-energy absorption bands in the near-UV region (200–300 nm) for these compounds are ascribed to the \(\pi\rightarrow\pi^*\) LC transition, while the lower energy bands correspond to the \(\text{d}(\text{Re})\rightarrow\pi^*(\text{diimine})\) MLCT transitions. The \(^1\)MLCT and \(^1\)LC excited states can be populated simultaneously. The presence of a heavy atom like rhenium in organometallic compounds increases spin-orbit coupling (SOC) and thereby favors intersystem crossing (ISC) from the singlet to the lowest triplet state (\(T_1\)). The \(T_1\) state is responsible for the radiative de-excitation process of \(T_1\rightarrowS_0\) (Scheme 1).\(^18\)

As a rule, the \(^3\)MLCT emitters exhibit broad, structureless emission bands, whereas an appreciable \(^3\)LC contribution leads to the appearance of a vibronic progression in the emission profiles. The \(^3\)MLCT and \(^3\)LC states often have comparable energies and therefore their mixture accounts for the photophysical behavior of rhenium luminophores.

**Scheme 1.** The state energy diagrams. \(^1\)MLCT and \(^1\)LC are the lowest excited singlet states, \(^3\)MLCT and \(^3\)LC are the lowest excited triplet states, \(k_{\text{ISC}}\) is the intersystem-crossing rate constant, \(k_r\) and \(k_{nr}\) are the radiative and non-radiative rate constants, respectively.\(^19\)

Strong ILCT electronic transitions often originate in complexes that contain extended donor-acceptor (D-A) diimines as chelating ligands. The charge transfer characteristics
depend on the energy levels of both donor and acceptor units, and can be fine-tuned by altering one or both of them or by modulating the donor-acceptor communication. The co-existence of reducing- and oxidizing ligands in rhenium(I) complexes gives rise to a low-lying LLCT excited state, by virtue of charge transfer from the donor (ancillary ligand that predominantly accommodates the highest occupied molecular orbital, HOMO) to the acceptor (diimine, where the lowest unoccupied molecular orbital, LUMO, is localized). The large structural distortion of the excited state and its low energy typically lead to a fast non-radiative deactivation process, making the \(^3\)LLCT states very short-lived. The LLCT states, which are “dark” in general, are mainly studied by transient spectroscopy or indirectly by analyzing their influence on the MLCT excited state lifetimes of the emissive species.\(^{17,21}\)

In general, the electronic properties and the physical behavior of rhenium(I) coordination compounds can be substantially influenced by changing the nature of the ligand environment. In other words, variations of the non-carbonyl bidentate as well as the ancillary ligands considerably affect the photoluminescence energies, lifetimes, and quantum efficiencies; thereby allowing delicate tuning of the photophysical properties.

1.2 Diimine rhenium(I) complexes: Diimine variation

Many studies have tried to establish the relationships between the structure/composition and the electronic/photophysical characteristics of luminescent rhenium(I) species. A majority of these studies focus on the photophysics and photochemistry of rhenium(I) diimine complexes.

Compounds of the general formula \([\text{Re}(\text{NN})(\text{CO})_3X]\) are conventionally prepared by heating \([\text{Re}(\text{CO})_5X]\) in the presence of the corresponding diimine. These carbonyl derivatives are probably the most extensively investigated family of Re complexes during the last 40 years, due to their facile synthesis, high stability, and tunability of the photophysical characteristics by accessible modification of the diimine ligand.

In 1974, Wrighton and Morse published a pioneering report on the photophysics of rhenium(I) systems based on 1,10-phenanthroline and related ligands. They demonstrated that those chromophores undergo efficient radiative relaxation in their lowest electronically excited state. The observed luminescence characteristics suggested that the emission is associated with the \(\text{Re} \rightarrow \pi^*(\text{diimine})\) charge transfer state. In addition, the luminescence lifetimes and the quenching experiments were largely consistent with the triplet \(\rightarrow\) singlet character of the radiative transition. The authors also described the unusual phenomenon of luminescence rigidochromism—a strong dependence of the emission energy on the rigidity of the environment.\(^8\)

In the mid-1980s, Kalyanasundaram presented a thorough account on the absorption and emission properties of a series of polypyridyl Re(I) complexes, and studied the sensitivity of their photophysical characteristics to changes in the polypyridyl ligand
and solvent. Namely, electron-donating substituents in the diimine structure induced moderate hypsochromic shifts of the low-energy absorption and emission bands, compared with complexes based on the polypyridyl ligands bearing electron-withdrawing substituents (Figure 2).

**Figure 2.** Shift of the emission to changes in the polypyridyl ligands in complexes 1–5 in CH$_2$Cl$_2$.\textsuperscript{22}

Furthermore, increasing the solvent polarity led to an obvious blue-shift in the absorption. The shorter emission lifetimes and reduced quantum yields in more polar solvents were ascribed to an increased rate of non-radiative decay to the ground state.

In the early 1990s, Demas and coworkers embarked on a detailed study of the isonitrile rhenium(I) photosensitizers [Re(CO)$_3$(NN)(NC(CH$_2$)$_n$CH$_3$)]$^+$, obtained by substituting the chloride ion in the [Re(CO)$_3$(NN)Cl] species with the isonitrile ligand. The isonitrile complexes showed extremely high luminescence quantum yields up to 80% and long lifetimes of greater than 130 µs at room temperature, illustrating the possibility to adjust the photophysical properties of rhenium(I) complexes by varying the ancillary ligands. The given synthetic approach demonstrated that accessible structural variations of these types of compounds permit the design of systems with remarkable optical behavior.\textsuperscript{23}

Functionalization of the diimine ligands remains a popular strategy in the molecular design of novel rhenium(I) luminophores. The rhenium-based phosphors exhibiting circularly polarized luminescence are notable examples of this methodology (Figure 3). The incorporation of rhenium ion into an extended helical $\pi$-conjugated bipyridine has a profound effect on the chiroptical and photophysical properties of the organic motif, leading to unprecedented circularly polarized phosphorescence.
Figure 3. Synthesis of rhenium(I) complexes 6 and enantio-enriched 7: (i) Re(CO)$_5$Cl, toluene, reflux; (ii) AgCF$_3$SO$_3$, EtOH/THF, then 2,6-dimethylphenyl isocyanide, THF, NH$_4$PF$_6$, 75–80%; (iii) AgBF$_4$, CH$_3$CN, reflux, then pyridine, THF, 80%.$^{24}$

Although the d$_{Re}$ orbitals do not strongly interact with the electronic π-systems of the helical polyaromatic fragments, coordination of the metal increases the π-conjugation area and promotes charge transfer excitations within the extended diimine ligand.$^{24}$

An interesting case of dramatic alteration in the emission energy was observed for two isomeric triazole-based rhenium(I) complexes, which contain two forms of the C$_2$N$_3$ heterocycle and consequently different dispositions of the 2-phenylbenzoxazole substituents. As a result of these stereochemical alterations, the emission band of 8 in solution is bathochromically shifted by 2390 cm$^{-1}$ (82 nm) with respect to 9 (Figure 4). Theoretical calculations pointed out that 8 has a smaller HOMO-LUMO gap than 9, in line with the experimental observations.$^{25}$

Figure 4. Absorption (black dotted lines), excitation (blue lines), and emission (red and green lines) spectra of complexes 8 (top) and 9 (bottom) in dichloromethane; photographs show the solutions under UV excitation, $\lambda = 365$ nm.$^{25}$
An impressive case of prolonged excited state lifetime was found in the rhenium(I) complex bearing the modified 1,10-phenanthroline with the naphthalimide moiety (Figure 5). The equilibrium between the lower $^1$LC state of the phen-based diimine and the $^3$MLCT emitting states greatly extended the excited state lifetime from 197 ns for the parent Re(phen)(CO)$_3$Cl to 651 µs for complex 10, but retained the same quantum yield (1.3%).

![Figure 5](image)

**Figure 5.** Proposed energy level diagram describing the photophysical processes of 10 in solution at room temperature. Empty arrow: absorption, filled arrow: radiative transition, and wavy arrow: non-radiative transition.

Rhenium complexes with bipolar chromophore scaffolds are photophysically diverse species featuring intraligand charge transfer. The use of donor-functionalized diimines promoted population in the low-lying ILCT states that are lower in energy than the MLCT states.

In a series of compounds based on dppz-type ligands (Figure 6), the spectroscopic properties were dominated by strong ILCT transitions from the electron-donating amino groups to the electron deficient dppz moiety, while the MLCT transitions were not perceptible. Unlike the non-coordinated functionalized diimines, these complexes were weakly emissive.

![Figure 6](image)

**Figure 6.** Schematic representation of complexes 11, 12$^{14}$ and 13, 14$^{20}$ featuring ILCT processes.

The luminescent complexes 15–18 with substituted 1,10-phenanthroline retained the dominating ligand-centered nature of the low-energy electronic transitions. However, it was noted that enhancing the electron withdrawing properties of the auxiliary ligand leads to a significant red-shift of the emission (Figure 7).
Evidently, careful design of diimine ligands, which themselves act as organic dyes, provides precious means for efficient modulation of the physical behavior of rhenium(I)-containing luminophores.

Thus, the majority of reported rhenium complexes are represented by either well-studied $^3\text{MLCT}$ chromophores or weakly luminescent emitters with diverse nature in their excited state ($\text{MLCT/ILCT}$, $\text{MLCT/LC}$, $\text{ILCT}$, and $\text{LC}$).

### 1.3 Diimine rhenium(I) complexes: Variation of ancillary ligands

In addition to the versatile variations of the diimine framework, changing the ancillary ligands also proved to be another feasible way to influence the physical and chemical properties of rhenium diimine species. As a consequence, a large number of these derivatives bearing carbenes, alkynyl-, cyano/isocynano-, and thiolate groups, phosphines, and N-heterocycles have been synthesized. In particular, a relatively simple modification of the neutral P- and N-donor ligands along with straightforward coordination chemistry offers a convenient pathway to tune the steric and electronic properties of the target rhenium(I) chromophores.

#### 1.3.1 Phosphine derivatives

Three practical synthetic methods have been described for preparing the mono- and disubstituted phosphine rhenium(I) complexes:

1) photochemical substitution;
2) thermal substitution;
3) carbonyl removal using trimethylamine $N$-oxide.

Originally, Wrighton discovered that 436-nm irradiation of the deoxygenated acetonitrile solution of $\text{[Re(CO)\textsubscript{3}(phen)(CH\textsubscript{3}CN)]\textsuperscript{+}}$ containing $\text{PPh\textsubscript{3}}$ and $[n-\text{Bu\textsubscript{4}}\text{N}]\text{PF\textsubscript{6}}/[n-\text{Bu\textsubscript{4}}\text{N}]\text{ClO\textsubscript{4}}$ led to formation of the tricarbonyl species $\text{[Re(CO)\textsubscript{3}(phen)(PPh\textsubscript{3})]}\textsuperscript{+}(\text{PF\textsubscript{6}}/\text{ClO\textsubscript{4}})^\text{-}$.
In 2000, the group of Ishitani presented a series of dicarbonyl compounds 
$[\text{Re}(\text{NN})(\text{CO})_2(\text{PR}_3)(\text{L})]^+$ (L = NCCH$_3$, py, PR$_3$), which were generated 
photochemically from the monosubstituted precursor $[\text{Re}(\text{NN})(\text{CO})_3(\text{PR}_3)]^+$ using 
higher-energy excitation ($\lambda > 330$ nm). This protocol has been particularly suitable for 
the synthesis of dicarbonyl complexes that contain two different phosphine ligands.\textsuperscript{35} 
Importantly, the reaction can be performed in a two-step manner, first producing the 
labile acetonitrile intermediates $[\text{Re}(\text{NN})(\text{CO})_2(\text{PR}_3)(\text{CH}_3\text{CN})]^+$, which can be further 
thermally converted into a range of heteroleptic derivatives.

A decade later, the same group used photochemical substitution to synthesize a family 
of diimine rhenium(I) complexes bearing two phosphine ligands with a variable 
number of phenyl groups, and studied the related photophysical processes.

Figure 8. Rhenium(I) complexes 19–25 with variable number of alkyl and/or phenyl 
groups on the phosphine ligands and their emission spectra.\textsuperscript{37}

Upon increasing the number of phenyl substituents $N_{\text{Ph}}$ from 0 to 6, the intensity of the 
$\pi-\pi^*$ absorption band at around 260 nm was enhanced, and a blue-shift from 427 to 
402 nm was observed for the MLCT absorption. Simultaneously, this structural 
alteration resulted in visible growth in both the emission energies (Figure 8) and 
quantum yields to 600 nm and 9%, respectively.\textsuperscript{37}

An alternative synthetic route was suggested by Sullivan, who synthesized dicarbonyl 
rhenium(I) complexes with monodentate or chelating phosphines via a thermal 
substitution reaction. A new class of long-lived luminescent compounds was prepared 
by refluxing either neutral [Re(CO)$_3$Cl] or cationic [Re(CO)$_3$(NN)(CF$_3$SO$_3$)] starting
materials with a stoichiometric amount of the appropriate phosphine (Scheme 2). All the obtained complexes were emissive in the range of 600–640 nm.\(^{42}\)

Scheme 2. Routes to the phosphine-diimine dicarbonyl rhenium complexes (i: o-dichlorobenzene, reflux; ii: AgOTf, dichloromethane).\(^{42}\)

Another pathway towards the phosphine-containing dicarbonyl halide complexes of rhenium(I) was presented in 2015 by Felton and co-authors (Figure 9). It involves treatment of \([\text{Re(CO)}_3\text{(NN)PR}_3](\text{PF}_6)\) species with 15 equiv. of tetraethylammonium chloride (NEt\(_4\)Cl) in the presence of 1 equiv. of trimethylamine N-oxide. This non-photochemical ligand substitution should be generally applicable for preparing light-sensitive Re(I) diimine carbonyl compounds.\(^{43}\)

Figure 9. Synthesis of rhenium(I) complexes 26–33 using trimethylamine N-oxide.\(^{43}\)

The influence of axial ligands on the electronic structures and optical properties of related rhenium(I) systems showed that, in complexes 34–37, substitution of the acetonitrile ligand by chloride and that of the carbonyl ligand by a phosphine led to significant bathochromic shifts of the absorption and emission bands (Figure 10).\(^{44}\)
**1.3.2 Nitrogen-donor derivatives**

At the end of the 1980s, Zipp, Demas, and DeGraff described various rhenium diimine complexes decorated with substituted pyridines. These compounds of the general composition \([\text{Re}(\text{NN})(\text{CO})_3\text{L}](\text{ClO}_4)\), where \(\text{L} = \text{substituted pyridine}\), were synthesized by refluxing the starting chloride precursors \([\text{Re}(\text{NN})(\text{CO})_3\text{Cl}]\) with excess amount of the appropriate pyridine in the presence of AgClO_4. A detailed study of the photophysical properties showed that the auxiliary pyridine derivatives exerted some noticeable influence on the luminescence behavior, although the effect was less pronounced than that caused by modification of the diimine ligands. For example, small shifts of the emission bands as well as minor changes in the luminescence lifetimes were observed.\(^{38}\)

Variation of the ancillary ligands in the coordination sphere of rhenium complexes can be realized by modification of the pyridine ligands after their coordination to the metallocenter. For instance, the weakly emissive diamine parent species \([\text{Re}(\text{CO})_3(\text{NN})(3,4\text{-diaminopyridine})](\text{CF}_3\text{SO}_3)\) was converted into the triazole counterparts by reacting with gaseous NO (Figure 11). As a result, an substantial emission enhancement was observed, meaning that rhenium(I) complexes \(38–41\) could be considered as sensors for nitric oxide (NO).\(^{40}\)

**Figure 10.** Left: synthesis of rhenium(I) compounds \(34–37\) (i: AgOTf, CH₃CN, 295 K, then \([\text{NH}_4][\text{PF}_6]\); ii: AgOTf, acetone, reflux, then PMe₃, acetone, reflux, after \([\text{NH}_4][\text{PF}_6]\); iii: Me₃NO, CH₃CN, reflux; iv: [BnMe₃N]Cl, CH₂Cl₂, reflux). Right: their absorption (solid lines) and emission (dashed lines) spectra in CH₃CN.\(^{44}\)
Figure 11. Conversion of 3,4-diaminopyridine complexes 38–41 into their triazolopyridine derivatives 42–45. Thus, the introduction of an additional chromophore center or a functional group into the axial position of rhenium(I) diimine unit may be an easy way to produce emissive materials with particular activities, e.g. luminescent probes.

In this respect, there is a keen interest in rhenium compounds containing ligands capable of reversible photoisomerization (e.g. trans→cis) due to their potential uses as photoinduced molecular sensors and switches. For example, the cis-isomers of complexes with 4-styrylpyridine are luminescent showing broad and poorly structured emission profiles, while the majority of the trans–forms undergo nonradiative relaxation of the excited state. Upon excitation, the photochemical reaction could proceed through the population of 1,3 MLCT Re→diimine state and the subsequent intramolecular energy transfer to 1IL trans–L (photoswitchable ancillary ligand) state (triplet pathway), or population of the 1IL trans–L state (singlet pathway). Highly efficient trans→cis isomerization (81%) was obtained for rhenium compound 46 by irradiation at 365 nm (Figure 12).

Figure 12. Spectral changes of complex 46 in CH₃CN under 356-nm irradiation.
1.4 Polynuclear complexes built from rhenium(I) diimine blocks

The multimetallic compounds constitute an interesting class of efficient luminophores. The construction of such assemblies is commonly based on a “complexes-as-ligands” concept. In this approach, a di- or polydentate bridging ligand binds the metal cores in a stepwise fashion. The nature of the linker and the coordination mode strongly influence the electronic communication between the constituting fragments. For weak interactions, the photophysical behavior combines properties of the two independent chromophore centers. In the case of strong interactions, the compounds can be considered as delocalized electronic systems with characteristics completely different from their monomeric analogs. The vast majority of reported multi-chromophoric rhenium metal complexes are based on \{Re(\text{NN})(\text{CO})_3\} units, because of their unique electronic and steric properties. By changing the linked metal components together with the stereochemistry of bridging ligands, it is possible to rationally tune the photophysical and photochemical characteristics.

1.4.1 Homometallic rhenium(I) complexes

The first work devoted to the synthesis of dinuclear homometallic complexes of rhenium(I) dated from the beginning of 1990s. Kalyanasundaram described the homonuclear cyano-bridged polypyridyl complex \[(\text{CO})_3(\text{bpy})\text{Re–CN–Re(bpy)}(\text{CO})_3\]^+\, obtained by reaction between the triflate precursor \[\text{Re(bpy)(CO)}_3(\text{CF}_3\text{SO}_3)\] and the cyanide complex \[\text{Re(bpy)(CO)}_3(\text{CN})\], which served as a metalloligand. It was found that the charge transfer absorption band in the dinuclear complex was blue-shifted and considerably broadened, with molar absorptivities being nearly two times larger than those of the parent mononuclear species. Both the mono- and dinuclear complexes displayed luminescence with single exponential decay, indicating that there was no separate emissions from two different chromophores\(^{32}\).

Later, Yam presented a dinuclear rhenium(I) compound containing a bridging butadiynyl ligand. The target complex \(^{47}\) (Figure 13), synthesized by cross-coupling two \[\text{Re(}t\text{Bu}_2\text{-bpy)}(\text{CO})_3(\text{C≡C})_2\text{H}\] units in the presence of \(\text{Cu(OAc)}_2\), demonstrated long-lived red emission from the \(^3\text{MLCT} \,(d\pi(\text{Re})\rightarrow\pi^*(t\text{Bu}_2\text{-bpy}))\) excited state. Interestingly, upon excitation at \(\lambda \geq 450\) nm, an emission band appeared in the NIR region and was assigned to \(^3\text{MLCT} \,(d(\text{Re})\rightarrow\pi^*(\text{C≡C})_2)\) or \(^3\text{LLCT} \,(\pi(\text{C≡C})_2\rightarrow\pi^*(t\text{Bu}_2\text{-bpy}))\) transitions.\(^{46}\).
Figure 13. Dirhenium(I) complex 47 with the acetylenic bridging ligand. Complexes 48 and 49 (Figure 14) exemplify a dinuclear architecture, where the rhenium fragments are connected through a flexible bridging bis-diimine ligand. In low-polarity solvents, these neutral compounds exhibited an unusual folded conformation due to the interaction between the amide and one rhenium-carbonyl group.

Figure 14. Synthesis of the flexible bridging ligands and the corresponding dirhenium(I) complexes 48 and 49: (i) 1,2-bis(2-aminoethoxy)ethane, NEt₃, dry THF, stirring, 16 h; (ii) [Re(CO)₅Br], toluene, reflux, 16 h. It was observed that the quantum yields of the complexes were dramatically affected by the substitution pattern within the diimine ligand. Introducing two electron-withdrawing groups into the 2,2’-bipyridine motifs turned the weakly luminescent complex 48 into the non-emissive system 49.

A substantial contribution to the development of supramolecular chemistry of rhenium complexes was made by the group of Ishitani, who developed a strategy to synthesize series of linear- and ring-shaped molecular assemblies. Polynuclear structures were constructed by linking the rhenium fragments {Re(CO)₂(NN)} with the bidentate phosphine (PP) ligands. Depending on the flexibility of the PP diphosphines, two main aggregation scenarios were realized: oligomerization of the linear rhenium(I) systems and oligonuclear cycle formation. For instance, a multistep synthesis of the trinuclear Re(I) ring with a rigid bridging PP ligand is illustrated in Scheme 3.
Scheme 3. Synthesis of the trinuclear Re(I) ring (PP = rigid bidentate phosphine ligands; \(i\): hv (\(\lambda > 330\) nm), acetone/H\(_2\)O; \(ii\): CH\(_3\)CN; \(iii\): acetone, reflux).\(^{49}\)

It is essential that these phosphine-bridged molecular assemblies are triplet emitters, whose photophysical characteristics are remarkably improved by the strong interligand \(\pi-\pi\) interactions. Specifically, in the Re-rings with ethynylene-containing PP ligands, interactions between the unsaturated chains and the bpy ligands resulted in a 3-fold enhancement of the emission intensity compared with analogues with alkyl fragments.\(^{38-50}\)

### 1.4.2 Heterometallic rhenium(I) complexes

The appealing physical properties and rather facile coordination chemistry of rhenium(I) diimine blocks determined their popularity in the construction of heterometallic assemblies. A variety of d- and f-metals were connected to the Re(I) chromophore by means of diverse ligand systems to extend the optical functionality of the target supramolecular compounds.

In the beginning of the 2000s, Lee and co-workers utilized a coordination-driven assembly approach for the synthesis of luminescent heterometallic palladium(II) (50–52) and platinum(II) (53, 54) tetranuclear square-like complexes (Figure 15).
Their photophysical properties were dominated by the conjugated bridging ligands. It was found that squares 50–54 comprising rigid ligands demonstrated weaker luminescence than that predicted by the energy gap law. The small quantum yields were interpreted in terms of quenching via Pt(II)- or Pd(II) oxidation, and energy transfer from the emitting $^3$MLCT state to lower-lying non-emissive states localized on the ferrocene groups.\textsuperscript{51}

Yam described bichromophoric polypyridine alkynyl-bridged molecular rods consisting of rhenium and platinum fragments (Figure 16). These complexes were prepared by coupling $[\text{Re(NN)(CO)}_3(\text{C}≡\text{C-(C}_6\text{H}_4)_n\text{-C}≡\text{CH})]$ and $[\text{Pt(NNN)}\text{Cl}(\text{CF}_3\text{SO}_3)]$ compounds, where NNN = terpyridine derivatives, in the presence of CuI and the base Et$_3$N.

All dyads displayed orange to red photoluminescence both in fluid media and in the solid state. The emission energies of complexes 55–58 were similar irrespectively of the nature of the substituents on the diimine ligand on the rhenium(I) metal. It was assumed that the observed emissions occur from the $^3$MLCT excited states, d\textsubscript{(Pt)}→$\pi^*$\textsubscript{(NNN)}, perturbed by the rhenium diimine fragment and perhaps mixed with
the LLCT $\pi(\text{C}=\text{C}-\text{R}) \rightarrow \pi^*(\text{NNN})$ or the metalloligand-to-ligand charge transfer $\pi(\text{C}=\text{C}-\text{C}_6\text{H}_4-\text{C}=\text{C}) \rightarrow \pi^*(\text{NNN})$.\textsuperscript{52} Unlike compounds \textsuperscript{55–58}, the mixed-metal rhenium(I)–gold(I) families \textsuperscript{59–62} (Figure 17) displayed luminescence assigned to the \(^1\)MLCT $d(\text{Re}) \rightarrow \pi^*(\text{NN})$ excited state.

![Figure 17](image)

**Figure 17.** Chemical structures of gold(I)–rhenium(I) systems with metallocenters linked through the ancillary (\textsuperscript{59–62})\textsuperscript{53} and diimine (\textsuperscript{63} and \textsuperscript{64})\textsuperscript{54} ligands.

The lack of emission from the alkynylgold(I) unit was explained by the efficient intramolecular energy transfer from the gold(I) to the rhenium(I) moiety.\textsuperscript{53,54} Similar energy transfer processes arose in the dinuclear [Re(phen)(CO)$_3$(μ-CN)Ir(F$_2$ppy)$_2$(CN)] and trinuclear [(Re(phen)(CO)$_3$(μ-CN)$_2$Ir(F$_2$ppy)$_2$](PF$_6$) rhenium(I)-iridium(III) systems, in which the chromophore units were linked by the cyanide bridges.\textsuperscript{55} A different situation was described for the linear multinuclear rhenium systems connected to a ruthenium fragment by a bis-diimine ligand (Figure 18). In this case, energy transfer occurred from the rhenium unit (a photon absorber) to the ruthenium motif (energy acceptor). Therefore, the emission behavior of these heterometallic oligomers was mostly determined by the Ru(II) motif.\textsuperscript{56}

![Figure 18](image)

**Figure 18.** The Ru(II)-Re(I) multinuclear complexes \textsuperscript{65–67}.\textsuperscript{56}
1.5 Applications

Feasible modulation of the photophysical properties along with the functionalities and reactivity of rhenium(I) complexes has made them candidates for a range of practical applications.

1.5.1 Organic light emitting diodes (OLEDs)

One of the strategies to achieve high-performance OLEDs is to utilize phosphorescent compounds that have the intrinsic advantage of maximum (100%) internal quantum efficiency of electroluminescence.

Thermally stable mononuclear rhenium(I) compounds with efficient luminescence have been used as transition metal complexes in the fabrication of phosphorescent OLEDs. Li and co-workers designed neutral Re(I) systems that showed significantly improved electroluminescent properties and exhibited strong electrogenerated emission (Figure 19). Complex 70 has a maximum current, power, external quantum efficiency, and CIE coordinates of 36.5 cd A⁻¹, 31.7 lm W⁻¹, 12.0%, and (0.46, 0.52), respectively. An EL device based on it was among the best orange OLEDs with rhenium(I) dopant emitters reported so far.

Figure 19. Structures of complexes 68–70 used as dopant emitters in electroluminescent devices.

1.5.2 Sensors

Luminescent rhenium(I) complexes containing recognition units that interact with analytes have emerged as a versatile class of molecular sensors. The examples of rhenium-based probes are designed for selective determination of metal cations. The chelating coordination function in the ancillary (Figure 20A) or diimine ligand (Figure 20B) of the rhenium chromophores makes them responsive to the presence of selected divalent metal cations. The complexation of Cd(II) or Zn(II) ions by the tetrazolato-quinoline ligands blue-shifts the emission of the rhenium(I) compound 71, and causes a substantial increase of phosphorescence intensity and elongation of the emission lifetimes. Similarly, the addition of Cu(II) ion to the chemosensor 72 leads to a significant enhancement in the emission intensity and
excited state lifetime of the Re(I) complex due to the suppression of C=N isomerization. \cite{67}

**Figure 20.** A: Complexation of complex 71 with Zn(II), and the corresponding photographs of CH$_2$Cl$_2$ solutions of 71 before and after the addition of Zn(II) salt. \cite{70} B: Complexation of complex 72 with Cu(II). \cite{67}

### 1.5.3 Photo-activated carbon monoxide releasing molecules (PhotoCORMs)

Recently, a promising approach to the controlled delivery of CO molecules for therapeutic applications is using carbonyl organometallic compounds, which are stable in the dark in aqueous solution for an extended period of time to afford sufficient accumulation in the target biological structures.

The low toxicity and tunable properties of Re(I)-based carbonyls ensured their growing usage as PhotoCORMs. \cite{71-74} For example, the photolytic liberation of carbon monoxide from complex 73 (Figure 21) is accompanied by a change of the orange phosphorescence (605 nm) to blue fluorescence (400 nm). This allows one to track the entry and delivery of this CO donor within the target localization. \cite{72}
1.5.4 Electrocatalysis

High-performance catalysts can facilitate reduction of CO$_2$ emission into the environment. The advantages of utilizing rhenium(I) complexes for electrocatalytic and photocatalytic reductions are first and foremost determined by the availability of at least two oxidation states, the presence of accessible coordination site(s), as well as high selectivity in the conversion of CO$_2$ to CO.$^{75-77}$ Water solubility played a substantial role in the development of compound 74 as an electrocatalytic system for the reduction of CO$_2$, where aqueous solutions acted as the electron source. The titled complex was used as a molecular catalyst in the electrochemical cell for CO$_2$-to-CO conversion (Figure 22), which proceeded with high total faradaic efficiency (81%) and high selectivity of CO$_2$ reduction (98%) even in acidic solution.$^{75}$

Figure 22. Schematic illustration of the full electrochemical cell for CO$_2$-to-CO conversion.$^{75}$
1.5.5 Bio-imaging

The major reason of exploiting triplet emissive rhenium(I) compounds with the general formula $[\text{Re(diiimine)(CO)}_3(L)]^{0/+}$ as cellular imaging probes is that their photophysical properties are mainly guided by the bidentate diimine ligand. Thus, the cellular uptake and localization properties of these complexes can be conveniently adjusted via functionalization of the monodentate auxiliary ligand L without affecting the luminescence behavior.78–81

Rhenium(I) complex 75 containing a fructose pendant group displayed the appropriate photoluminescent characteristics ($\lambda_{\text{em}} = 553$ nm, $\tau = 2.9$ µs, $\Phi = 18\%$ in phosphate-buffered saline) as well as high cell permeability and organelle selectivity. It was successfully applied for imaging breast adenocarcinoma cell lines (Figure 23). Additionally, the given compound exhibited photocytotoxic activity caused by $\text{^1O}_2$ generation upon irradiation at $\lambda>365$ nm, making it an efficient photodynamic therapy agent.82

Figure 23. Confocal images of four different types of cancer cells upon incubation with complex 75 (50 µM, 1 h) at 310 K.82
1.6 Aims of the study

The rational design and synthesis of rhenium(I) carbonyl species with adjustable electronic parameters and tailored functional groups are very important for prospective applications that require molecular materials with certain photophysical and chemical behavior. The foregoing survey of literature data shows that the diimine ligands generally play a key role in the photophysics of the archetypal rhenium-based systems of [Re(CO)₃(NN)(L)]. Therefore, electronic changes of the NN constituents are primarily responsible for variation in the optical characteristics of rhenium derivatives. However, it is clear that their luminescence can also be substantially influenced by altering the ancillary ligand(s) or by coupling the emissive Re(I) motifs with additional chromophore units.

My research focused on the development of rhenium-based luminescent compounds, with an aim of establishing the relationship between their structures and photophysical properties. The chosen molecular design relied on the electronic and stereochemical modifications of the constituting fragments, following the strategy summarized in Scheme 4.

Scheme 4. Illustration of the research objectives.
(I) The first objective deals with the methodological approach to efficiently luminescent rhenium dicarbonyl compounds that are axially substituted with ancillary phosphine ligands having variable donor ability and the conjugated substituents.

(II) In the second task, I considered systematic alteration of the new type of diimine ligands tailored to the secondary chromophore system for constructing bichromophore rhenium dyes containing donor–acceptor organic motifs.

(III) In the third direction, the rhenium diimine tricarbonyl block was utilized to design series of homo- and heterometallic assemblies through merging two or more metal-based chromophores. Here, I intended to investigate two approaches, in which the target polynuclear compounds would differ in the rigidity and degree of conjugation between luminescent units.
All reactions (except the heterometallic systems described in publication IV) were performed under an inert atmosphere of nitrogen using standard Schlenk techniques.

2.1 Syntheses

2.1.1 Ligands

Commercially available diimines (1,10-phenanthroline (phen) and 2,2’-bipyridine (bpy)) and aminopyridines (4-aminopyridine (pyN1), 4-(aminomethyl)pyridine (pyN2), 4-(2-aminoethyl)pyridine (pyN3)) were used as received. Ancillary alkynyl-phosphine ligands (P1, P4, PP1, and PP2) were prepared according to the published procedures, which involve lithiation of the terminal alkynes and subsequent treatment with diphenylchlorophosphine (Scheme 5). The novel phosphines P2, P3, P5, and P6 were obtained following this general protocol as described in publication I.

Scheme 5. Synthesis of alkynyl-phosphine ligands: (i) n-BuLi dropwise, Et₂O/hexane, 195 K, stirring, 5 min, then 243 K, 1.5 h; (ii) PPh₂Cl dropwise, 195 K, stirring, then 298 K, stirring, 12 h; (iii) PPhCl₂ dropwise, 195 K, stirring, then 298 K, stirring, 2 h.

2.1.2 Metal complexes

Neutral rhenium(I) complexes [Re(NN)(CO)₃Cl] (NN = bipyridine, phenanthroline) were prepared according to the literature procedure by reacting the corresponding diimine with the commercially available pentacarbonyl [Re(CO)₅Cl]. The cationic starting materials [Re(NN)(CO)₃(NCMe)](CF₃SO₃) and [Re(NN)(CO)₃(H₂O)](CF₃SO₃) were obtained by treating their rhenium(I) chloride precursors with AgCF₃SO₃ in acetonitrile and wet acetone solvents, respectively.

To prepare the heterobimetallic Re–Pt species presented in publication III, the labile platinum compounds Pt(ppy)Cl(dmso) and [Pt(dpyb)(acetone)](CF₃SO₃) were obtained as described in the corresponding literature.
All novel homo- and heterometallic rhenium(I) complexes summarized in Table 1 were synthesized using the general approaches of coordination chemistry. The details are given in the original publications I–IV and in the following chapters.
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2.2 Characterization

All novel complexes were studied in solution by NMR and FT-IR spectroscopies and ionization electrospray mass spectrometry (ESI-MS). Most of the rhenium compounds in Table 1 were isolated as crystalline materials suitable for single-crystal X-ray diffraction analysis. Their molecular structures in the solid state were in agreement with spectroscopic data obtained in the fluid medium. The only exception was the complex ReAuPPh₃–phen (publication IV), which demonstrated reversible dissociation and rearrangement in solution as confirmed by NMR and ESI-MS measurements. Phase identification of the ReAuPPh₃–phen crystalline material was carried out by X-ray powder diffraction analysis. The purity of the studied species was confirmed by microanalyses carried out at the analytical laboratory of the University of Eastern Finland.

The photophysical measurements (UV/vis absorption, excitation and emission spectra, excited state lifetimes, and emission quantum yields) for all titled compounds were carried out using the core facilities of St. Petersburg State University and the scientific equipment of Peter the Great St. Petersburg Polytechnic University with the support of Dr. Alexei Melnikov.

Supplementary magnetic and electrochemical studies were performed by collaborating groups at RWTH Aachen University, Germany (Prof. Kirill Monakhov, now at Leibniz Institute of Surface Engineering) and University of Valencia, Spain (Prof. Antonio Doménech-Carbó). The computational analysis was done at the University of Eastern Finland (Dr. Pipsa Hirva, MSc. Toni Eskelinen) and Aalto University, Finland (Prof. Antti J. Karttunen).
3 RESULTS AND DISCUSSION

3.1 Alkynylphosphine rhenium(I) complexes

The prototype moiety \{Re(CO)\textsubscript{3}(phen)\}, which generally offers high luminescence efficiency\textsuperscript{15,91} but often suffers from limited photostability,\textsuperscript{92–94} was utilized for constructing robust rhenium phosphine-disubstituted platform. An expeditious route to the target complexes relied on the displacement of carbonyl ligands in the metal coordination sphere by thermally stable phosphines under extreme temperature conditions. Luminescence behavior of the final Re(I) compounds was modulated through the extension of conjugated substituents in the alkynylphosphine ligands.

The family of monodentate \textit{P}\textsubscript{1–P6} and bidentate \textit{PP}1 and \textit{PP}2 phosphine ligands were readily obtained following a conventional protocol shown in Scheme 6. Alkynylphosphines were incorporated into the coordination sphere of rhenium(I) species by one-step thermal substitution, reacting \([\text{Re(CO)}\textsubscript{3}(\text{phen})(\text{NCMe})](\text{CF}_3\text{SO}_3)\) compound with excess amount of the corresponding P-donor ligand. Following this strategy, phosphine dicarbonyl rhenium(I) complexes \textbf{Re(P1)\textsubscript{2}} – \textbf{Re(P6)\textsubscript{2}}, \textbf{(RePP1)\textsubscript{2}}, and \textbf{(RePP2)\textsubscript{2}} were generated using an autoclave technique under a nitrogen pressure of 30 atm. For selective isolation of the disubstituted species, the synthetic route was performed under optimized conditions, where the mononuclear complexes were obtained at 175–200 °C, while dinuclear congeners required elevated temperatures (220 °C). Note that in contrast to the titled complexes with mono- and dialkynylphosphines, no target compounds bearing the trialkynylphosphines \textbf{P}(C≡CR)\textsubscript{3} (R = Ph, biphenyl) were obtained due to degradation of the reagents.

\textbf{Scheme 6.} Synthesis of the alkynylphosphine dicarbonyl rhenium(I) complexes.

All rhenium(I) complexes are air- and moisture-stable compounds. Single-crystal XRD analysis was carried out for \textbf{Re(P1)\textsubscript{2}}–\textbf{Re(P3)\textsubscript{2}} and \textbf{(RePP1)\textsubscript{2}} species for unequivocal identification of their molecular structures. These dicarbonyl compounds revealed octahedral coordination geometry of the metal centers. The phosphine ligands are located at the axial positions, i.e. above and below the equatorial plane defined by the phenanthroline fragment and the CO groups (Figure 24), in line with the previous studies.\textsuperscript{35–37} A visible deviation of the P–C≡C fragments from linear structure (with angles of 162–179°) is eventually induced by intermolecular interactions in \textbf{Re(P1)\textsubscript{2}}–\textbf{Re(P3)\textsubscript{2}} and \textbf{(RePP1)\textsubscript{2}}, and is not exceptional.\textsuperscript{36,37}
In solution, the synthesized phosphine ligands and the related complexes were unambiguously characterized by NMR, FT-IR, and ESI-MS spectroscopic methods.

For all complexes, two intense IR bands at 1880–1896 and 1950–1963 cm\(^{-1}\) were attributed to symmetric and asymmetric stretching vibrations of the two adjacent CO groups. The C≡O stretches in Re(P4)\(_2\)–Re(P6)\(_2\) occurred at higher frequencies in comparison with those in Re(P1)\(_2\)–Re(P3)\(_2\), due to decreased electron density on the Re(I) centers caused by the more π–accepting phosphines. The \(^1\)H and \(^31\)P NMR spectroscopic patterns reflected the presence of a symmetrical stereochemical environment around the central rhenium atom in the final compounds.

All rhenium(I) species were intensely luminescent, with the emission mainly determined by \(^7\)MLCT rhenium→diimine electronic transitions (Table 2), as is typical for the rhenium(I) chromophores.\(^{8,95,96}\)

In dichloromethane solutions at ambient temperature, the positions of the absorption and emission maxima as well as the luminescence intensity of rhenium(I) complexes (Re(P1)\(_2\)–Re(P6)\(_2\), (RePP1)\(_2\), and (RePP2)\(_2\)) were virtually identical, pointing to the innocent character of the phosphines with respect to the energies of the electronic transitions. Referenced to the previous spectroscopic investigations of related Re(I) systems,\(^{36,37,97,98}\) the phosphorescence quantum yields of the titled family are among the highest (up to 44\%) for reported phosphine-containing emitters.

In contrast to the solution medium, the solid-state photophysical characteristics of the described rhenium-based systems were affected by the ancillary alkynylphosphines.
Figure 25. Normalized emission spectra of the crystalline complexes Re(P1)$_2$–Re(P3)$_2$ and Re(P1)$_2$ in solution (CH$_2$Cl$_2$) at 298 K.

For instance, the emission bands were gradually red-shifted upon extending the phenylene chain in the phosphine ligands (Figure 25). Owing to the phenomenon of luminescence rigidochromism,$^{99–101}$ a blue-shift in the solid state relative to the solution was observed for this series of rhenium(I) emitters.

Table 2. Photophysical properties of complexes Re(P1)$_2$–Re(P6)$_2$, (RePP1)$_2$, and (RePP2)$_2$ in solution (CH$_2$Cl$_2$) and in the solid state at 298 K.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{abs}}$, nm ($\varepsilon$, $10^4$ M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$, nm</th>
<th>$\lambda_{\text{em}}$, nm</th>
<th>$\Phi$, % (aer/degas)</th>
<th>$\tau$, µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(P1)$_2$</td>
<td>271 (2.9), 298 (1.8), 384 (0.4)</td>
<td>608</td>
<td>533</td>
<td>15/34</td>
<td>1.04</td>
</tr>
<tr>
<td>Re(P2)$_2$</td>
<td>295 (4.0), 383 (0.3)</td>
<td>608</td>
<td>562</td>
<td>17/34</td>
<td>1.03</td>
</tr>
<tr>
<td>Re(P3)$_2$</td>
<td>274 (2.7), 313 (5.3), 383 (0.3)</td>
<td>607</td>
<td>577</td>
<td>15/30</td>
<td>1.03</td>
</tr>
<tr>
<td>Re(P4)$_2$</td>
<td>277 (3.4), 300 (1.9), 382 (0.4)</td>
<td>601</td>
<td>581</td>
<td>17/42</td>
<td>0.99</td>
</tr>
<tr>
<td>Re(P5)$_2$</td>
<td>297 (6.3), 310 (6.6), 379 (0.6), 415 (0.4)</td>
<td>601</td>
<td>588</td>
<td>16/44</td>
<td>0.97</td>
</tr>
<tr>
<td>Re(P6)$_2$</td>
<td>275 (4.6), 325 (8.2), 410 (0.4)</td>
<td>601</td>
<td>619</td>
<td>10/27</td>
<td>0.98</td>
</tr>
<tr>
<td>(RePP1)$_2$</td>
<td>277 (6.4), 295 (7.4), 410 (0.7)</td>
<td>600</td>
<td>598</td>
<td>11/30</td>
<td>1.08 (90 %), 0.30 (10 %)</td>
</tr>
<tr>
<td>(RePP2)$_2$</td>
<td>274 (5.2), 316 (9.0), 408 (0.7)</td>
<td>610</td>
<td>608</td>
<td>7/13</td>
<td>0.23 (26 %), 0.90 (74 %)</td>
</tr>
</tbody>
</table>

$^a$CH$_2$Cl$_2$ solution ($\lambda_{\text{ext}}$, 385 nm). $^b$Solid state.

To provide further insight on the optical properties, quantum chemical analysis was carried out for the electronic structures. The calculation results for complexes
**Re(P1)₂−Re(P6)₂** show some overestimation of the absorption and emission wavelengths, while the simulated $T_1 \rightarrow S_0$ emission wavelengths for complexes (RePP₁)₂ and (RePP₂)₂ are rather close to the experimental data (Table 3).

**Table 3.** Computational estimation of the photophysical properties for complexes Re(P₁)₂−Re(P₆)₂, (RePP₁)₂, and (RePP₂)₂.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{abs} S_0 \rightarrow S_1$, nm</th>
<th>$\lambda_{em} T_1 \rightarrow S_0$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(P₁)₂</td>
<td>438 (0.01)</td>
<td>661</td>
</tr>
<tr>
<td>Re(P₂)₂</td>
<td>446 (0.01)</td>
<td>669</td>
</tr>
<tr>
<td>Re(P₃)₂</td>
<td>477 (&lt;0.01)</td>
<td>623</td>
</tr>
<tr>
<td>Re(P₄)₂</td>
<td>435 (0.04)</td>
<td>680</td>
</tr>
<tr>
<td>Re(P₅)₂</td>
<td>448 (0.02)</td>
<td>689</td>
</tr>
<tr>
<td>Re(P₆)₂</td>
<td>470 (0.01)</td>
<td>687</td>
</tr>
<tr>
<td>(RePP₁)₂</td>
<td>459 (0.23)</td>
<td>615</td>
</tr>
<tr>
<td>(RePP₂)₂</td>
<td>467 (0.25)</td>
<td>628</td>
</tr>
</tbody>
</table>

* Oscillator strengths are given in parentheses.

For all rhenium(I) species, the corresponding transitions are mainly of $d\pi(Re)−\pi^(*)\text{(phen)}~1,1\text{MLCT}$ character, with negligible contributions from the alkynyl fragments of the phosphines to the emissive excited states (Figure 26).
38

Figure 26. Electron density difference plots for the lowest-energy singlet excitation (S₀→S₁) of systems Re(P1)₂, Re(P4)₂, and (RePP2)₂. During the electronic transition, the electron density increases in the blue areas and decreases in the red areas.

Research discussed in this section focused on the new phosphine-substituted rhenium complexes to improve their photoluminescence properties. Although the ancillary phosphine ligands showed little influence on the emission energy in solution, they clearly affect the behavior in the solid state. Moreover, the developed synthetic approach demonstrates a quite facile route to the rhenium compounds with high quantum efficiency and remarkable stability, which are the prominent advantages of these systems over most of other rhenium emitters.

3.2 Rhenium(I) complexes based on the extended diimine ligands

One of the approaches to alter the photophysical properties of rhenium(I)-based molecular architectures relied on the coordination of the presynthesized chromophore diimines to the metal center.²⁰,²⁵,¹⁰² For this purpose, the pyridyl-phenanthroimidazole core was selected as the ligating unit due to its straightforward synthesis and functionalization, as well as efficient binding toward the transition metal ions.¹⁰³ Integration of secondary chromophore moieties into the aforementioned bidentate platform was anticipated to tune the optical properties of the resulting [Re(CO)₃(NN)Cl] species.

Modular platforms NN₁ and NN₂, conventionally prepared by Debus-Radziszewski condensation reaction, were converted into the bichromophore compounds NN₃–NN₅
containing electron-rich anthracene-derived functional groups via Sonogashira cross-coupling reaction (Scheme 7).

Scheme 7. Synthesis of NN1–NN5 and schematic structures of rhenium complexes ReNN1 to ReNN5 and ReNN1-CN.

The target tricarbonyl complexes ReNN1–ReNN5 were obtained following the standard procedure. Exchange of the chloride ligand by cyanide was accomplished by chloride abstraction with silver cyanide to give the compound ReNN1-CN.

In accordance with the X-ray crystallographic studies of NN1 and NN5, the nearly flat phenanthro-imidazole fragment was almost perpendicular to the N-bounded phenyl ring, which probably diminished the conjugation between the polyaromatic units in the bichromophore ligands NN3–NN5. The coordination of the bulky diimines to the rhenium(I) metallocenter through the pyridyl-imidazole chelating moiety caused steric hindrance between the equatorial carbonyl ligand and the adjacent H–C group of phenanthrene. The result was substantial geometry distortion that shifted the metal atom out of the plane of the diimine. In all these complexes (ReNN1 to ReNN5 and ReNN1-CN), the rhenium ions had the distorted octahedral environment typical for the tricarbonyl diimine compounds (Figure 27).
Spectroscopic measurements confirmed that the given diimine ligands and the corresponding complexes retained their structures in solution. Particularly, the $^1\text{H}$ NMR spectra demonstrated a number of clearly resolved multiplets in the aromatic region that pointed to the stereochemical rigidity of the titled compounds (Figure 28).

Figure 27. Molecular views of the complex ReNN5.

Figure 28. $^1\text{H}$ NMR spectra of the ligand NN2 and complexes ReNN2 (400 MHz, DMSO-$d_6$, 298 K).
The photophysical studies of these species mainly concerned their solution behavior (Table 4, Figures 29–31). The extended π-conjugated phenanthrene skeleton endowed NN1 and NN2 with \(1 \pi^*\)phenanthrene LC fluorescence, which was virtually invariant to the \(para\)-substituent in N-bounded phenyl ring. Both ligands produced similar vibronically structured deep blue emission with a maximum at around 380 nm and the quantum yields of 37% and 22%, respectively. Tailoring various anthracene-containing units to the phenanthro-imidazole core differentiated NN3, NN4, and NN5 chromophores according to their optical properties.

![Normalized emission spectra of NN1–NN5 (solid lines) and ReNN5 (dotted line) (CH\(_2\)Cl\(_2\), 298 K).](image)

**Figure 29.** Normalized emission spectra of NN1–NN5 (solid lines) and ReNN5 (dotted line) (CH\(_2\)Cl\(_2\), 298 K).

Compound NN3 displayed luminescence nearly identical to that of reported anthracene derivatives,\(^{107,108}\) with a quantum efficiency of 62%. Expansion of the \(\pi\)-system and introduction of the electron-donating groups in dyes NN4 and NN5 changed the character of the electronic transitions and significantly decreased the optical band gap.\(^{20,109,110}\) In \(\text{CH}_2\text{Cl}_2\) solutions, NN4 and NN5 showed highly intense structureless \(1\)ILCT luminescence (\(\Phi_{em}\) up to 92%) in the yellow (566 nm) to orange (602 nm) region. Moreover, diimines NN4 and NN5 exhibited distinct fluorescence solvatochromism attributed to the intramolecular charge transfer due to their donor-acceptor (D-A) architecture.\(^{20,111–113}\) The emission bands of the latter displayed substantial red shifts with increasing solvent polarity from cyclohexane to DMF (Figure 30A).

The N-donor functions in NN1–NN5 enabled reversible switching of the photophysical properties by protonation, which was also confirmed by NMR spectroscopy. For instance, upon treating NN1 with CF\(_3\)COOH, the luminescence spectrum showed two new broad bands at ca. 413 and 517 nm that were bathochromically shifted with respect to the initial signal (380 nm). This observation was attributed to the protonation of the pyridyl-imidazole site, which presumably activated the emissive \(1\)ILCT phen→py excited state.\(^{114}\)
Figure 30. (A) Normalized emission spectra of NN5 at 298 K in various solvents, with the inset showing their visual appearance under UV light ($\lambda_{\text{ext}} = 365$ nm). (B) Effect of protonation on the photoemission spectrum of NN5 ($c = 10^{-5}$ M, CH$_2$Cl$_2$, 298 K).

The protonation site, which mainly affected the optical characteristics in NN5, was the N$_{\text{amino}}$ donor. The addition of CF$_3$COOH to a solution of NN5 (Figure 30B) converted the broad $^1$ILCT emission band centered at 602 nm to the structured $^1\pi\pi^*$ anthracene LC fluorescence band at around 490 nm. The original luminescence of the titled compounds was restored upon neutralizing the acid with a stronger base, e.g. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

Table 4. Photophysical properties of ligands NN1 to NN5 and related complexes ReNN1 to ReNN5 and ReNN1-CN in solution (CH$_2$Cl$_2$, 298 K).

<table>
<thead>
<tr>
<th></th>
<th>$^a\lambda_{\text{em}}$, nm</th>
<th>$^a\Phi$, %</th>
<th>$\tau$, ns</th>
<th>$^a\lambda_{\text{em}}$, nm</th>
<th>$^a\Phi$, %</th>
<th>$\tau$, ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN1</td>
<td>370, 388</td>
<td>37</td>
<td>1.9</td>
<td>ReNN1</td>
<td>369, 392, 408, 616</td>
<td>2 (616 nm)</td>
</tr>
<tr>
<td>NN2</td>
<td>370, 388</td>
<td>22</td>
<td>1.9</td>
<td>ReNN2</td>
<td>371, 392, 407, 624</td>
<td>2 (624 nm)</td>
</tr>
<tr>
<td>NN3</td>
<td>433, 459, 486</td>
<td>65</td>
<td>3.3</td>
<td>ReNN3</td>
<td>436, 460, 486(sh)</td>
<td>3</td>
</tr>
<tr>
<td>NN4</td>
<td>446w, 475w, 566</td>
<td>52</td>
<td>2.1 (446 nm) 1.4 (566 nm)</td>
<td>ReNN4</td>
<td>572</td>
<td>10</td>
</tr>
<tr>
<td>NN5</td>
<td>484w, 602</td>
<td>92</td>
<td>2.6 (484 nm) 3.8 (602 nm)</td>
<td>ReNN5</td>
<td>614</td>
<td>22</td>
</tr>
</tbody>
</table>

$^a\lambda_{\text{ext}} = 260$ nm (NN1, NN2), 360 nm (NN3), 365 nm (NN4, NN5, ReNN1 to ReNN5, and ReNN1-CN).
In the fluid medium, coordination compounds ReNN1 to ReNN5 and ReNN1-CN demonstrated moderate photoluminescence with $\Phi_{\text{em}}$ up to 22%. Remarkably, the excitation of ReNN1 and ReNN2 gave rise to dual luminescence, with two bands at ca. 400 and 620 nm corresponding to $^1$LC and $^3$ML'LCT origins, respectively (Figure 31). The proposed assignment was based on the strikingly different dependence of the intensity of these bands on the presence of molecular oxygen and the shapes of the emission profiles. Notably, the phenomenon of dual emission is scarce among rhenium(I) diimine systems.\textsuperscript{115–118}

**Figure 31.** Normalized emission spectra of ReNN1-CN and ReNN2, the corresponding spectrum of NN2 (filled) is shown for comparison (degassed CH$_2$Cl$_2$, 298 K).

In the case of ReNN1-CN, the dual luminescence disappeared, apparently as a result of a change in the nature of the emissive excited state from mainly $^3$ML'LCT to the mixture $^3$(LC+ML'LCT). Compared to ReNN1, ReNN1-CN revealed a blue-shifted (by 34 nm, 950 cm$^{-1}$) and poorly structured emission profile (Figure 31) together with a 10-fold increase in quantum efficiency (from 2% to 20%).

Interestingly, complexes ReNN3–ReNN5 demonstrated optical characteristics that are very similar to those of the parent ligands NN3–NN5 (Figure 29). This observation implied that the emissions of ReNN4 and ReNN5 were dominated by the $^1$ILCT transitions, which was also confirmed by the sensitivity to protonation and to the solvent polarity. In contrast, most of previously reported rhenium(I) luminophores principally displayed $^3$MLCT/$^3$IL emission\textsuperscript{105,119} or demonstrated the formation of dark $^3$ILCT state,\textsuperscript{14,120} which fundamentally distinguish them from ReNN3–ReNN5 complexes showing relatively efficient intra-ligand fluorescence.

These results illustrated that the pyridyl-imidazole core combined with tricarbonyl rhenium(I) unit can produce complexes with versatile photophysical properties. Compounds ReNN1 and ReNN2 displayed excitation-dependent singlet/triplet dual emission, while changing the ancillary X ligand switched the luminescence of ReNN1-CN to exclusively triplet in origin. The $^1$ILCT emissive states, which are unconventional for rhenium luminophores, were realized for ReNN4 and ReNN5.
species by using the extended ligands with secondary chromophore fragments of a donor-acceptor nature. Furthermore, this family of chromophore-functionalized diimines can potentially serve as useful building blocks to generate complexes of many other transition metals.

3.3 Bichromophore rhenium(I)–platinum(II) complexes based on the rhenium(I) aminopyridine predecessors

Another direction in the development of di-component emitters was compounds comprising both the rhenium(I) and platinum(II) phosphorescent units. Tethering the emissive cycloplatinated fragments \(\{\text{Pt}(ppy)\text{Cl}\}\)\textsuperscript{121,122} and \(\{\text{Pt}(dpyb)\}\textsuperscript+\textsuperscript{90,123}\) to the \(\{\text{Re(phen)}(\text{CO})_3\}\) chromophore was achieved by utilizing the bifunctional aminopyridine ligands with different lengths in the spacers. This approach assumed that the photophysical features of each component are preserved in the bichromophore complex.

The preparation of rhenium(I) complexes \(\text{Re(pyN}_1\text{)}\)–\(\text{Re(pyN}_3\text{)}\) relied on site-selective coordination of the heterodentate aminopyridines to the \([\text{Re(CO)}_3(\text{phen})(\text{NCMe})](\text{CF}_3\text{SO}_3)\) precursor (Scheme 8).

Scheme 8. Synthesis of the aminopyridine rhenium complexes and the rhenium(I)–platinum(II) complexes.

The \(^1\text{H NMR}\) spectra showed a distinct difference in chemical shifts of the low-field signals of the diimine protons for \(\text{Re(pyN}_1\text{)}\) and the pair \(\text{Re(pyN}_2\text{), Re(pyN}_3\text{)}\), consistent with two types of coordination of aminopyridines to the Re(I) center. As
indicated by X-ray crystallography data (Figure 32), linking pyN1 to rhenium diimine unit occurred through the pyridine N-donor, while pyN2 and pyN3 were bonded to the metal through the primary amine group. It should be noted that the N\textsuperscript{amine} coordination mode has been found in only a few cases of Re(I) complexes.\textsuperscript{124,125}

The mononuclear rhenium complexes Re(pyN1)–Re(pyN3) were \textsuperscript{3}MLCT-type emitters (Figure 33 and Table 5), similar to other rhenium(I) species with the ancillary N-heterocycles.\textsuperscript{38,40,126} Re(pyN1) displayed a bathochromic shift of the emission maximum (by 10 nm) and reduced quantum efficiency (around 2 times) with respect to Re(pyN2) and Re(pyN3), while the photophysical characteristics of the latter two complexes were almost identical. However, in the solid phase, the different rigidity of the crystal packing led to the dissimilar photophysical behaviors of these rhenium congeners (Table 5).

![Figure 32. Molecular views of complexes Re(pyN2)Pt(dpyb) and Re(pyN3)Pt(ppy). CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} counter ions were omitted for clarity.](image)

Further construction of bimetallic complexes Re(pyN2)Pt(ppy), Re(pyN2)Pt(dpyb), Re(pyN3)Pt(ppy), and Re(pyN3)Pt(dpyb) was achieved by merging Re(pyN2)/Re(pyN3) predecessors with the platinum(II) building blocks via N\textsuperscript{py} vacant coordination function of the aminopyridine ligands (Scheme 8). The compositions and structures of the dinuclear assemblies were established by means of IR and NMR spectroscopies, ESI-MS, and X-ray crystallography. The single-crystal structures confirmed the assembly of the heterometallic cations Re(pyN2)Pt(ppy), Re(pyN2)Pt(dpyb), Re(pyN3)Pt(ppy), and Re(pyN3)Pt(dpyb). These assemblies consisted of the distorted octahedral rhenium moieties and the square-planar platinum fragments bridged by pyN2 and pyN3 (Figure 32). Thus, spatially separated metal ions appeared in their typical geometries.\textsuperscript{122,126–128} The solution \textsuperscript{1}H NMR spectroscopic data of the rhenium(I)–platinum(II) architectures clearly indicated retention of the molecular structures in solution.
Table 5. Photophysical properties of complexes Re(pyN1)–Re(pyN3), Re(pyN2)Pt(ppy), Re(pyN2)Pt(dpyb), Re(pyN3)Pt(ppy), and Re(pyN3)Pt(dpyb) in solution (CH$_2$Cl$_2$) and in the solid state at 298 K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{abs}}$, nm ($\varepsilon$, 10$^4$ M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$, nm</th>
<th>$^{a}\Phi$, % (aer/degas)</th>
<th>$^b\tau$, µs</th>
<th>$^{b}\Phi$, %</th>
<th>$^{b}\tau$, µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(pyN1)</td>
<td>360 (0.4), 271 (4.6), 262 (4.4)</td>
<td>580</td>
<td>6/14</td>
<td>0.7</td>
<td>550</td>
<td>9</td>
</tr>
<tr>
<td>Re(pyN2)</td>
<td>362 (0.3), 324 (0.5), 276 (2.1), 258 (2.0)</td>
<td>570</td>
<td>15/29</td>
<td>1.5</td>
<td>517</td>
<td>20</td>
</tr>
<tr>
<td>Re(pyN3)</td>
<td>360 (0.3), 322 (0.5), 275 (2.0), 257 (2.0)</td>
<td>570</td>
<td>14/25</td>
<td>1.4</td>
<td>571</td>
<td>4</td>
</tr>
<tr>
<td>Re(pyN2)Pt(ppy)</td>
<td>376 (0.5), 340 (0.9), 324 (1.1), 275 (3.5), 258 (4.2), 247 (3.8)</td>
<td>566</td>
<td>6/10</td>
<td>0.5 (85%)</td>
<td>1.4 (15%)</td>
<td>479, 502, 516, 537</td>
</tr>
<tr>
<td>Re(pyN2)Pt(dpyb)</td>
<td>399 (0.5), 377 (0.8), 361 (0.7), 329 (1.0), 278 (3.4), 256 (3.6)</td>
<td>$^{f}8/17$</td>
<td>2.7</td>
<td>490, 525, 565, 611</td>
<td>2</td>
<td>$^{d}0.6$</td>
</tr>
<tr>
<td>Re(pyN3)Pt(ppy)</td>
<td>371 (0.5), 340 (0.8), 324 (1.0), 274 (3.6), 257 (4.5), 249 (4.2)</td>
<td>570</td>
<td>4/8</td>
<td>0.4 (88%)</td>
<td>1.3 (12%)</td>
<td>492, 526, 555</td>
</tr>
<tr>
<td>Re(pyN3)Pt(dpyb)</td>
<td>400 (0.6), 378 (0.8), 363 (0.7), 330 (1.0), 287 (2.6), 276 (3.1)</td>
<td>$^{f}8/28$</td>
<td>1.6</td>
<td>493, 600</td>
<td>5</td>
<td>490, 525, 561, 611</td>
</tr>
</tbody>
</table>

$^a$CH$_2$Cl$_2$ solution ($\lambda_{\text{ext}}$ 365 nm). $^b$Solid state. $^c$Average emission lifetimes for the two exponential decays determined by the equation: $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$; $A_i$ is the weight of the $i$-th exponent. $^d$Rhenium fragment. $^e$Platinum fragment. $^f$c$_{\text{max}} = 1.7\times10^{-5}$ M for Re(pyN2)Pt(dpyb) and 1.2$\times10^{-5}$ M for Re(pyN3)Pt(dpyb).

Different from reported heterometallic species with "antenna"-type constituting fragments,129–131 these complexes (Re(pyN2)Pt(ppy), Re(pyN2)Pt(dpyb), Re(pyN3)Pt(ppy), and Re(pyN3)Pt(dpyb)) demonstrated reasonably efficient $^3$MLCT photoluminescence with quantum yields up to 28%. The luminescence behavior of bimetallic assemblies Re(pyN2)Pt(ppy), Re(pyN2)Pt(dpyb), Re(pyN3)Pt(ppy), and Re(pyN3)Pt(dpyb) was altered by means of the platinum-containing units, whilst contribution of the rhenium chromophores remained invariable (Table 5).

Re(pyN2)Pt(ppy) and Re(pyN3)Pt(ppy) in fluid media demonstrated phosphorescence, which included featureless rhenium-dominated emission with high-energy shoulders at ca. 490 nm of the weakly emissive platinum motif$^{132}$ (Figure 33).
Figure 33. Normalized emission spectra of complexes \( \text{Re(pyN1)} \), \( \text{Re(pyN2)} \), \( \text{Re(pyN2)Pt(ppy)} \), and \( \text{Re(pyN2)Pt(dpyb)} \) in solution (CH\(_2\)Cl\(_2\)) at 298 K.

The other pair of \( \text{Re(pyN2)Pt(dpyb)/Re(pyN3)Pt(dpyb)} \) species revealed a substantially increased contribution of the platinum chromophore to the observed emission. The key feature in both the absorption and emission spectra of \( \text{Pt(dpyb)} \)-containing assemblies was their concentration dependence. In dilute solutions, the emission profiles of \( \text{Re(pyN2)Pt(dpyb)} \) and \( \text{Re(pyN3)Pt(dpyb)} \) showed an intense high-energy band with clear vibronic progression that corresponds to the \{Pt(dpyb)\} unit, and a weaker red-shifted broad band of the \{Re(phen)\} chromophore (Figure 34A). For \( \text{Re(pyN3)Pt(dpyb)} \), apparent changes in the intensities of high- and low-energy emission bands upon concentration increase were accompanied by the appearance of a subtle shoulder at around 650 nm (Figure 34B). This new long-wavelength phosphorescence band was assumed to originate from intermolecular interactions.

Figure 34. A: Concentration dependence of the emission spectra of \( \text{Re(pyN3)Pt(dpyb)} \) in solution (CH\(_2\)Cl\(_2\)) at 298 K. B: Deconvolution of the emission spectrum of \( \text{Re(pyN3)Pt(dpyb)} \) at \( c = 6\times10^{-5} \) M into three independent bands.

In order to rationalize the possible aggregates, TD-DFT studies were performed to simulate the observed concentration-dependent alterations in the UV-visible spectra. In
contrast to the homoleptic {Re}−{Re} and {Pt}−{Pt} aggregates, the predicted absorption spectra for {Re(phen)}⋯{Pt(dpyb)} stacks reasonably agree with the experimental data, as evidenced from Figure 35. When the aromatic systems of {Re(phen)} and {Pt(dpyb)} fragments were separated by 3.4 Å (mimicking the association via π-stacking at higher concentrations), there is an intensity reduction for the lower energy absorption peak, in line with experimental data. This stacking model portrays an unprecedented case of heteroleptic π–π interaction involving platinum square planar complexes.

![Figure 35](image_url)

Figure 35. A: UV-vis absorption spectra of Re(pyN3)Pt(dpyb) at variable concentrations (CH2Cl2, 298 K). B: TD-DFT simulated absorption spectra of the {Re}−{Pt} intermolecular stacking motif to model the aggregation of complex Re(pyN3)Pt(dpyb).

The solid-state photophysical behavior of the rhenium(I)-platinum(II) architectures generally resembled the luminescent behavior in solution, expressed by a combination of emissions from both chromophoric metal centers.

In this study, I investigated the photophysical behavior of phosphorescent bichromophores by implementing the Re(I)−Pt(II) combination. The variation of the platinum cyclometalated fragments allowed tuning of the contributions of metal constituents to the observed emission. Importantly, the cationic complexes Re(pyN2)Pt(dpyb) and Re(pyN3)Pt(dpyb) demonstrated a concentration-dependent tendency to aggregate through unconventional π−π stacking heteroleptic interactions {Re(phen)}⋯{Pt(dpyb)}, which occur in the ground state and result in the appearance of panchromatic luminescence.

3.4 Multichromophore rhenium(I) complexes of different nuclearity

The synthesis of multichromophore Re(I) supramolecular structures was performed via a coordination-driven self-assembly route. The chosen molecular design featured terminal {Re(CO)3(phen/bpy)} units around the central [M(CN)y]1− scaffold (M = Au,
Pt, Fe; \( y = 2-6 \)). The nature of the assembling cyanometallates determined the nuclearity of the resulting coordination architectures.

The construction of the multinuclear structures was based on the "metalloligand" strategy, which consists of decorating the cyanide or cyanometallates by two or more rhenium(I) fragments \([\text{Re(CO)}_{3-x}\text{(phen/bpy)}(\text{PPh}_3)_x(\text{H}_2\text{O})]^+\) (\( x = 0, 1 \)) under mild conditions (Scheme 9).

\[
\text{Scheme 9. Synthetic approach to homo- and heterometallic rhenium(I) complexes. The detailed synthetic procedures are described in publication IV.}
\]

The stoichiometry of all compounds was confirmed by ESI-MS measurements. However, due to reduction of Fe\(^{3+}\) to Fe\(^{2+}\) under the ESI-MS conditions, the signal of triply charged cation \(\text{Re}_6\text{Fe}^{3-}\text{bpy}\) could not be detected. Nevertheless, the cyanide stretching frequencies of \(\text{Re}_6\text{Fe}^{2-}\text{bpy}\) and \(\text{Re}_6\text{Fe}^{3-}\text{bpy}\) in their IR spectra (at 2089 and 2154 cm\(^{-1}\), respectively) provided conclusive support for the existence of two different Fe centers. The different CN band frequencies could be explained by the different \(\pi\)-basicities of the iron centers. In the \(^1\text{H}\) NMR spectra of \(\text{Re}_2-\text{NN}\) and \(\text{Ph}_3\text{PRe}_2-\text{phen}\) (where NN = bpy, phen), the presence of two sets of diimine signals with 1:1 ratio suggests the formation of dyads with non-equivalent rhenium units. The \(^1\text{H}\) NMR spectroscopic profiles of \(\text{Re}_2\text{Au-NN}, \text{Re}_2\text{Pt-NN}, \text{and Re}_6\text{Fe}^m-\text{bpy}\) (\( m = 2, 3 \)) correspond to only one type of Re(I) fragments, indicating high symmetry of the architectures.
The obtained multinuclear complexes were analyzed by single-crystal XRD techniques. In all these assemblies, the metal atoms in the diimine rhenium units had a slightly distorted octahedral surrounding (Figure 36).\textsuperscript{137–139} The diimine and carbonyl ligands supplied five donor atoms, while the sixth coordination vacancy was filled with the cyanide group.

Two \{Re(phen)(CO)\textsubscript{3-x}(PPh\textsubscript{3})\textsubscript{x}\} fragments connected through the cyanide bridge in a nearly linear fashion afforded dimeric Re\textsubscript{2−phen} and Ph\textsubscript{3}PRe\textsubscript{2−phen} complexes. They adopt nearly eclipsed conformations along the Re-CN-Re axis (torsion angles < 3°), resembling that of previously reported Re\textsubscript{2−bpy}.\textsuperscript{32,139}

The structure of ReAuPPh\textsubscript{3−phen} revealed a heterobimetallic architecture, which consisted of neutral [Au(PPh\textsubscript{3})(CN)] and cationic \{Re(phen)(CO)\textsubscript{3}\}\textsuperscript{+} subunits held together by the cyanide.

In aggregates Re\textsubscript{2}Au−NN, Re\textsubscript{4}Pt−NN, and Re\textsubscript{6}Fe\textsubscript{2−bpy}, the central [M(CN)\textsubscript{y}]\textsuperscript{−} scaffolds (M = Au, Pt, Fe; y = 2−6) acted as anionic polydentate ligands toward the pendant \{Re(NN)(CO)\textsubscript{3}\} blocks (Figure 36).

Two \{Re(NN)(CO)\textsubscript{3}\} units were linked to one [Au(CN)\textsubscript{2}]\textsuperscript{−} core to form trinuclear species Re\textsubscript{2}Au−bpy and Re\textsubscript{2}Au−phen with eclipsed and staggered conformations, respectively. The resulting Re–NCAuCN–Re arrays deviated from linearity, with the Re(I)–Au(I)–Re(I) angles of 165.4–175.4°. Assemblies involving the anionic building block [Pt(CN)\textsubscript{4}]\textsuperscript{2−} formed square-like pentanuclear Re\textsubscript{4}Pt−bpy and Re\textsubscript{4}Pt−phen architectures. The decoration of [Fe(CN)]\textsuperscript{4−/3−} cores by six \{Re(CO)\textsubscript{3}(bpy)\} fragments
produced the almost spherical complexes $\text{Re}_6\text{Fe}^2\text{--bpy}$ and $\text{Re}_6\text{Fe}^3\text{--bpy}$. Each iron center adopted the expected octahedral geometry consisting of six C atoms from bridging cyanide ligands. Despite equivalence of the rhenium fragments in solution, in the crystal steric requirements of the diimine ligands caused certain deformations of the ideal arrangements of $\text{Re}_4\text{Pt--NN}$ and $\text{Re}_6\text{Fe}^m\text{--bpy}$ compounds.\textsuperscript{137,140,141}

All these homo- and heterometallic rhenium(I) complexes were good absorbers of visible light. With the exception of Re–Fe assemblies, they also featured relatively intense and long-lived luminescence associated with the triplet nature of the excited state (Table 6). In fluid media, compounds $\text{Re}_2\text{--NN}$, $\text{Re}_2\text{Au--NN}$, and $\text{Re}_4\text{Pt--NN}$ containing tricarbonyl rhenium moieties demonstrated green to yellow emission with quantum yields up to 48%. A hypsochromic shift of the emission maxima and systematic enhancement of the luminescence intensity were detected after replacing the bpy ligand for the related phen. This observation was in concordance with previously published data for $[\text{Re(NN)(CO)}_3\text{L}]$ emitters.\textsuperscript{22,142,143} In addition, phosphorescence bands of the phen-based chromophores showed stronger sensitivity to the presence of $\text{O}_2$ compared to the bpy-analogues. This might be due to the longer excited state lifetimes and larger size of the phenanathroline systems, making them more susceptible to collisional quenching.

Table 6. Photophysical properties of complexes $\text{Re}_2\text{--NN}$, $\text{Ph}_3\text{PRe}_2\text{--phen}$, $\text{ReAuPPh}_3\text{--phen}$, $\text{Re}_2\text{Au--NN}$, $\text{Re}_4\text{Pt--NN}$, and $\text{Re}_6\text{Fe}^m\text{--bpy}$ ($m = 2, 3$) in solution (CH$_2$Cl$_2$) and in the solid state at 298 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi$, % (aer/degas)</th>
<th>$\tau$, $\mu$s</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi$, %</th>
<th>$\tau$, $\mu$s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Re}_2\text{--bpy}$</td>
<td>287 (4.6), 315 (2.4), 368 (1.0)</td>
<td>571</td>
<td>7/10</td>
<td>0.4</td>
<td>523</td>
<td>19</td>
<td>1.0</td>
</tr>
<tr>
<td>$\text{Re}_2\text{--phen}$</td>
<td>260 (8.8), 287 (4.4), 355 (1.2)</td>
<td>564</td>
<td>12/30</td>
<td>1.6</td>
<td>528</td>
<td>22</td>
<td>2.5</td>
</tr>
<tr>
<td>$\text{Ph}_3\text{PRe}_2\text{--phen}$</td>
<td>267 (9.8), 321 (2.5), 456 (1.2)</td>
<td>737</td>
<td>$&lt;1$</td>
<td>0.023</td>
<td>637</td>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>$\text{ReAuPPh}_3\text{--phen}$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>534</td>
<td>25</td>
<td>2.4</td>
</tr>
<tr>
<td>$\text{Re}_2\text{Au--bpy}$</td>
<td>246 (8.4), 281 (4.7), 317 (2.9), 359 (1.1)</td>
<td>554</td>
<td>11/19</td>
<td>0.6</td>
<td>522</td>
<td>31</td>
<td>1.0</td>
</tr>
<tr>
<td>$\text{Re}_2\text{Au--phen}$</td>
<td>249 (9.6), 254 (9.5), 273 (7.7), 330 (1.6)</td>
<td>543</td>
<td>15/48</td>
<td>1.9</td>
<td>562</td>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>$\text{Re}_4\text{Pt--bpy}$</td>
<td>246 (10.3), 281 (9.0), 305 (5.7), 318 (5.1), 355 (1.8)</td>
<td>560</td>
<td>10/21</td>
<td>0.5</td>
<td>547</td>
<td>14</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{Re}_4\text{Pt--phen}$</td>
<td>257 (12.5), 274 (12.5), 338 (2.2)</td>
<td>549</td>
<td>12/42</td>
<td>2.2</td>
<td>549</td>
<td>19</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^a$CH$_2$Cl$_2$ solution ($\lambda_{\text{ext}}$ 365 nm). $^b$Solid state ($\lambda_{\text{ext}}$ 340 nm).
The \([\text{Au(CN)}_2]^-\) and \([\text{Pt(CN)}_4]^{2-}\) cyanometallate linkers did not significantly affect the photophysical behavior of the polynuclear rhenium(I) systems, which was clearly supported by DFT calculations (Figure 37). The conversion of tricarbonyl rhenium complex \(\text{Re}_2\text{phen}^{-}\) into dicarbonyl phosphine derivative \(\text{Ph}_3\text{PRe}_2\text{phen}^{-}\) shifted the emission to the near-IR region and decreased the quantum efficiency. In comparison to the literature precedents, \(\text{Ph}_3\text{PRe}_2\text{phen}^{-}\) is an uncommon example of structurally simple rhenium(I) NIR emitter.\(^{13,144,145}\)

Photophysical characteristics of the crystalline samples were very similar to those found in solution, indicating that the emissive excited state had the same origin in both phases. The DFT analysis underscored the nature of the low-energy electronic transitions, which are localized on the \([\text{Re(NN)(CO)}_3]\) fragments and principally correspond to the \(d_{\text{Re}} \rightarrow \pi^*_{\text{NN}}\) \(^3\)MLCT process (Figure 37).

![Figure 37](image)

**Figure 37.** Electron density difference plots of complexes \(\text{Re}_2\text{Au-phen} (S_0 \rightarrow S_1)\) and \(\text{Re}_4\text{Pt-bpy} (S_0 \rightarrow S_1)\). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas.

None of the Re–Fe complexes showed appreciable luminescence. In contrast to other aggregates where the \([\text{M(CN)}_y]\)\(^{n-}\) bridges were electronically innocent, the \([\text{Fe(CN)}_6]\)\(^{4-/3-}\) fragments played a major role in the lowest-energy excitation and therefore evidently provided non-radiative relaxation pathways, which account for the lack of emission.
The electrochemical and magnetic properties of $\text{Re}_6\text{Fe}^m\text{-bpy}$ were investigated. The complexes exhibited irreversible Re$^I$ to Re$^II$ oxidation along with a quasi-reversible reduction of $[\text{Fe}^{II/III}(\text{CN})_6]^{4-/3-}$ moieties. The magnetic data for compound $\text{Re}_6\text{Fe}^3\text{-bpy}$ clearly indicated a low-spin octahedral configuration of the Fe$^{III}$ ion, which is virtually unaffected by the coordination of terminal {Re(bpy)} blocks.

The described coordination-driven self-assembly of the Re(I) aggregates demonstrated an efficient synthetic route to supramolecular systems comprising several chromophore fragments. Depending on the electronic features of the connecting cyanometallate, optical properties of these polynuclear species are defined either by the rhenium diimine components, or by the central heterometal ion and the energy transfer between the constituents. Notably, despite their multichromophore nature that is often detrimental to luminescence, most of the studied compounds retain intense emission, which can be extended into the NIR region upon a simple modification of the ligand sphere.
4 CONCLUSIONS

In this work, I have investigated the structure-property relationships for a series of organometallic luminescent complexes based on the rhenium(I) diimine-carbonyl chromophore units. The prototype motif \([\text{Re(CO)}_3(\text{diimine})_L] \) (where \(L = \text{auxiliary ligand} \)) offers substantial synthetic freedom along with appealing optical characteristics. Therefore, it has been used to design several new families of Re(I)-containing emitters. In order to manipulate the behavior of the excited state, I implemented a number of stereochemical modifications that involve changes of the ligand coordination sphere and the combination of two or more chromophore units in one molecular entity.

As the first step, I studied the phenanthroline rhenium complexes, which incorporated alkynylphosphine ligands with different electron-donor strength and stereochemistry. In fluid medium, varying the alkynyl-phenylene substituents had negligible effect on the electronic absorption and emission energies of the final Re(I) systems. However, the incorporation of two phosphines into the diimine-dicarbonyl fragment led to high quantum yields and remarkable stability in comparison with conventional tricarbonyl systems. In contrast to the solution behavior, the solid-state emission spectra featured a gradual bathochromic shift upon extension of the phenylene chain in the phosphine substituents, which presumably influences rigidity of the environment of the chromophore motif.

In the second direction, I have employed phenanthrene imidazole-pyridyl moiety as a chelating diimine. The neutral rhenium(I) tricarbonyl derivatives displayed dual fluorescence/phosphorescence, which can be controlled by the excitation wavelength. The straightforward functionalization of this diimine with an additional fluorophore fragment changed the emission origin to the singlet intra-ligand character, which is not typical for Re(I) emitters. The energy of the corresponding electronic transitions was readily influenced by the donor-acceptor nature of the extended ligands, which resulted in the charge transfer emissive states. Consequently, the fluorescence of the parent dyes and their Re(I) compounds with electron-donating pendant groups exhibited pronounced red-shifts with increasing solvent polarity, indicating positive solvatochromic properties. Furthermore, optical properties of these emitters can be switched in the presence of a protonating agent in a reversible manner.

The third part of my research considered cationic dyads constructed from the Re(I) and Pt(II) chromophores and linked through the bifunctional aminopyridine ligands. These bimetallic systems might help clarify the delicate balance between preserving the independent performance of each component (i.e. maintaining dual emission) and the energy transfer between two different metal fragments. The cycloplatinated motifs were used to regulate the phosphorescent properties, whereas the emission characteristics of the rhenium centers remained unaltered in these assemblies. Remarkably, the heterometallic species based on the \{Pt(NCN)\} moiety displayed
concentration dependence in both the absorption and emission spectra, which was assigned to unusual $\pi$-stacking interactions of the heteroleptic type $\{\text{Re(NN)}\} \cdots \{\text{Pt(NCN)}\}$.

In the fourth chapter of the thesis, I designed multicomponent self-assemblies constructed from the Re(I) building blocks. The supramolecular architectures comprised two or more rhenium(I) fragments in tandem with the cyanometallates $[\text{M(CN)}_y]^{n-}$ ($\text{M} = \text{Au, Pt, Fe}; y = 2$–$6$) as bridging ligands. The photophysical properties of the gold and platinum-centered aggregates were governed by the nature of the diimine-rhenium platforms, while the nuclearity of the metal complexes had a minor influence on the absorption and emission behaviors. Interestingly, the polynuclear rhenium(I) emitters attained high luminescence with quantum efficiencies up to $48\%$, despite the presence of several photofunctional components.

In total, the judicious design of multichromophore structures offers wide opportunities for elegantly tuning of the photophysical properties of rhenium(I) diimine-based complexes. These complexes can be used to develop versatile luminescent molecular materials.
ACKNOWLEDGEMENT

This work was carried out at the Department of Chemistry, University of Eastern Finland during the years 2015-2019. Financial support provided by the Finnish National Agency for Education (CIMO Fellowship), the Academy of Finland and the University of Eastern Finland (SCITECO grant) is gratefully acknowledged.

Primarily, I would like to express my profound appreciation to my supervisor, Prof. Igor Koshevoy. His solid expertise, professional guidance and unwavering support during this period have been invaluable. I am indebted to my second supervisor, Assoc. Prof. Elena Grachova, for giving me opportunity to work on this project.

Secondly, I am most grateful to the group of Prof. Sergey Tunik (St. Petersburg State University), to Dr. Pipsa Hirva (UEF), to Prof. Antti Karttunen (Aalto University), to Dr. Alexei Melnikov (Peter the Great St.-Petersburg Polytechnic University) and to Ilya Kondrasenko for their resourceful and productive collaboration.

I would also like to extend my gratitude to all personnel at Department of Chemistry, especially to Prof. Tapani Pakkanen, Prof. Mika Suvanto, Dr. Sari Suvanto, Ms. Mari Heiskanen, Ms. Taina Nivajarivi, Ms. Paivi Inkinen and Ms. Eija Faari-Kapanen for their friendly cooperation and assistance during my doctoral studies.

Furthermore, I would like to acknowledge Prof. Risto Laitinen (University of Oulu) and Prof. Andreas Steffen (Technical University of Dortmund) for critically reading this thesis and for valuable comments.

Additionally, I sincerely thank my colleagues and friends, especially, Andrey Belyaev, Anastasia Solomatina and Julia Shakirova for their advice regarding my scientific work and for their immense encouragement over the years.

At last but not the least, I would like to extend the heartfelt thanks to my family, who are always by my side and give a precious counterbalance to the studies.

Joensuu, 2019

Kristina Kisel
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Probing the effect of coordination environment on the photophysical behavior of rhenium(I) luminophores