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Synthesis and Evaluation of Photoactive Pyridine Complexes for Electron Transfer Studies and Photoelectrochemical Applications

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Abstract
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In this thesis, the preparation of new photoactive substances containing mono- and bipyridines coordinated to ruthenium is presented together with initial evaluations of their photoelectrochemical and photophysical properties.

Complexes of the type $Ru(bpy)_2(4\text{-}X\text{-}py)_2$ (X = SH, COOH) were prepared and used in Grätzel-type solar cells based on ZnO. The results show that the thiol complex binds to the surface but give rather low solar cell efficiencies. Different routes to obtain $Ru(bpy)_2(4,4'\text{-dithio-}2,2'\text{-bipyridine})$ were evaluated, among them substitution reactions on 4,4′-dichloro-2,2′-bipyridine coordinated to ruthenium. Due to reactivity issues, the target sulphur-containing complex has not yet been obtained.

The synthesis of methanofullerenes, fulleropyrrolidines and –pyrazolines are presented, among them dyads containing $Ru(bpy)_n$-units. A common feature for the dyads is the unusually short linkers between the fullerene and the ruthenium complex. Dyad preparations were in some cases simplified by carrying out the reactions in the presence of silver salts.

A preliminary evaluation of the emission of the dyads showed almost complete quenching of the excited state of a pyrrolidine-based dyad, whereas emission remained from the pyrazoline-based ones. Whether this was due to incomplete quenching of the excited states of the ruthenium complex, or induced by the presence of hydrazones has yet to be revealed.

The use of fullerene-substituted malonic acid and its ethyl ester as dyes in Grätzel-type solar cells resulted in even lower efficiencies (IPCE) than for bare TiO_2. This could be due to electron transfer in the reverse direction compared to what is observed for ruthenium complexes. Thus, these fullerene derivatives are not suitable as sensitisers for Grätzel-type solar cells.

Keywords: Fullerene, solar cell, bipyridines, Ruthenium, organic synthesis

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List of papers

This thesis is based on the following papers:

I   Wallin, S.; Davidsson, J.; Modin, J.; Hammarström, L. Femtosecond Transient Absorption Anisotropy Study on $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)(py)_4]^{2+}$. Ultrafast Interligand Randomization of the MLCT State. *Journal of Physical Chemistry A* **2005**, *109*, 4697-4704.

II Ohlsson, J.; Wolpher, H.; Hagfeldt, A.; Grennberg, H. New dyes for solar cells based on nanostructured semiconducting metal oxides - Synthesis and characterisation of ruthenium(II) complexes with thiol-substituted ligands. *Journal of Photochemistry and Photobiology A: Chemistry* **2002**, *148*, 41-48.

III Modin, J.; Johansson, H.; Grennberg, H. New pyrazolino- and pyrrolidino[60]fullerenes with transition-metal chelating pyridine substitutents: Synthesis and complexation to Ru(II). *Organic Letters* **2005**, *7*, 3977-3979.

IV Modin, J.; Hammarström, L.; Grennberg, H. Dyads with Ru(II)(bipyridine)-based chromophores covalently attached to [60]fullerene *via* short pyrazolino- or pyrrolidino links. Synthesis and preliminary photophysical studies. *Preliminary manuscript*

V   Appendix: Modin, J. *Supplementary material*

Comments on my participation: (I) Synthesis of Ru(bpy)(py)$_4$·2PF$_6$; (II) made all the synthesis and measurements except the work regarding diazo compounds and wrote the paper; (III) was involved in all synthetic work and wrote the paper; (IV) made all the synthetic work, participated in the discussion and in writing.

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Contents

Abbreviations

AcCl	acetyl chloride
AcOH	acetic acid
bpy	2,2´-bipyridine
CB	conduction band
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	*N,N´*-dicyclohexylcarbodiimide
DMF	*N,N*-dimethyl formamide
DMSO	dimethylsulphoxide
e^-	electron
Et	ethyl
EtOH	ethanol
hv	photon
h	hour(s)
HOMO	highest occupied molecular orbital
IPCE	incident photon-to-current conversion efficiency
I_{sc}	short-circuit current
L	ligand
LDA	lithium diisopropyl amide
LUMO	lowest un-occupied molecular orbital
mCPBA	3-chloroperbenzoic acid
MW	microwave assisted heating
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NHE	normal hydrogen electrode
NMR	nuclear magnetic resonance
Ph	phenyl
py	pyridine
r.t.	room temperature
THF	tetrahydrofuran
UV	ultraviolet
VB	valence band
vis	visible
V_{oc}	open-circuit voltage

1   Objectives and outline

The Sun is the source to most life on Earth. It gives us light, warmth and food, but we ought to use more of what it is giving us.

The majority of the energy used in the world today is produced from fossil fuels and a global task is to find a solution to the equation of rapidly decreasing sources of such fuels, together with the increasing demands for energy. One alternative would be to develop the use of solar energy. Two ways of doing this, both subjects of extensive research, are the use of solar cells[1-4] or artificial photosynthesis.[5] Solar cells transform the sunlight into electricity while devices based on artificial photosynthesis should be able to split water into oxygen and hydrogen gas that in turn can be used as an environmentally friendly fuel, a concept still at the research stage. Although solar cells are commercially available, those found on the market today are mostly made from crystalline silicon and since high perfection and purity of the silicon crystals is required, such cells are still expensive. Therefore, development of cheap, but still efficient, solar cells is needed. Among several types,[1,2,6-8] the dye-sensitised Grätzel solar cell could fulfil these requirements.[9-14]

Both dye-sensitised solar cells and systems for artificial photosynthesis require molecules that absorb visible light and use the energy to transfer an electron to another part of the system. Such a molecule can be a complex between ruthenium and bipyridines, substituted in a suitable way and connected to an electron acceptor (a semiconducting oxide or a fullerene) *via* a linker, figure 1.
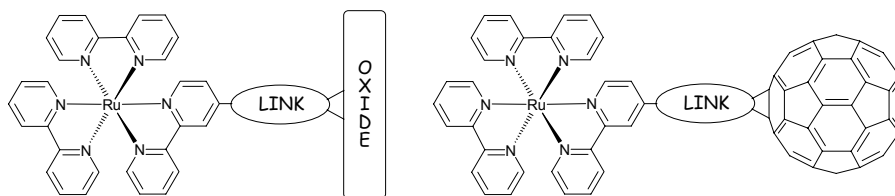

Figure 1. Schematic picture of $Ru(bpy)_n$ in two electron transfer systems.

This thesis concerns the preparation of substituted mono- and bipyridines, in some cases connected to fullerene C_{60}, to be coordinated to ruthenium. The aim was also to evaluate the properties of these complexes as dyes in dye-sensitised solar cells and their electron transfer abilities.

In Chapter 3 the synthesis of complexes of the type $Ru(bpy)_2(4\text{-}X\text{-}py)_2$ (X = SH, COOH) are discussed together with evaluation of how thiols function as linkers between the complex and the semiconductor, here ZnO, in Grätzel-type solar cells. The work to synthesise $Ru(bpy)_2(4,4´\text{-dithio-}2,2´\text{-bipyridine})$ is also presented. Chapter 4 concerns dyads between $Ru(bpy)_3$-complexes and fullerene C_{60}; the preparation of complexes, fullerene adducts and their combinations. It also discusses some photophysical characteristics for these substances.

2   Introduction

2.1   Bipyridine complexes of Ru^{II}

There is a variety of light absorbing, electron-donating molecules, many of them complexes between transition metals and organic ligands like bi- and terpyridines,[15,16] phenantrolines[17] and porphyrins.[18] There are some requirements a photoactive electron donor ought to fulfil such as (i) strong absorption of visible light to harvest as much energy as possible; (ii) the excited state should have a sufficiently long lifetime for the transfer of an electron to the acceptor to occur; (iii) a reversible redox behaviour to be able to repeatedly donate electrons, and (iv) the molecule should be relatively stable and easy to prepare. Complexes between 2,2′-bipyridine and ruthenium, osmium or rhenium are well-suited in these respects and are therefore among the most well-studied systems in photophysical processes.[15,16,19,20]

To be able to connect a bipyridine complex to an electron acceptor, semi-conducting or molecular, one of the ligands has to be functionalised. Nucleophilic substitution on free bipyridines takes place at 2- or 4- position relative to the nitrogens, while electrophilic substitution usually takes place at the 3- position. As bipyridines are electron-deficient aromatic compounds, rather harsh reaction conditions usually have to be used in order to succeed with the desired transformations.

Ruthenium-bipyridine complexes are generally prepared starting from RuCl$_3$. A common procedure to obtain bis-heteroleptic complexes, for example Ru(bpy)$_2$(η^2-L) **2**, is to reflux Ru^{III}Cl$_3$ and bipyridine in DMF to obtain Ru(bpy)$_2$Cl$_2$, **1**,[21] scheme 1. To increase the solubility of the Ru^{III}-salt, LiCl is added to the reaction mixture. The last step to obtain the desired complex is to exchange the two remaining chlorides for the ligand of choice, usually by refluxing the complex precursor and the ligand in ethanol or water. Sometimes slightly less polar solvents, like 2-methoxyethanol, are preferable if the ligand is not sufficiently soluble in ethanol. However, if the polarity is too high, the ruthenium salt **1** does not dissolve, resulting in a loss of reactivity.
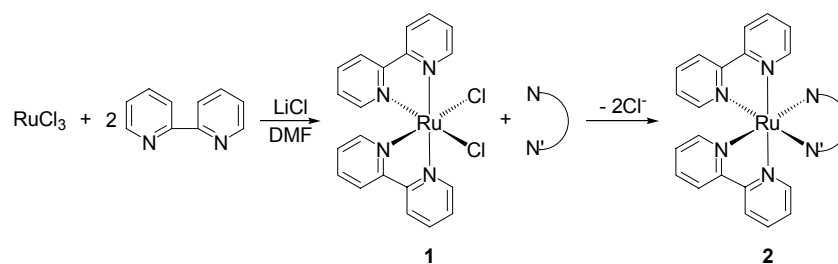
Scheme 1. Preparation of complexes of the type $Ru(bpy)_2(\eta^2\text{-}L)$, **2**.

If all the ligands are neutral, the resulting complex will bear two positive charges from the metal. Initially, the chlorides will function as counter-ions, but they are usually exchanged by larger anions like PF_6^-, BF_4^- and ClO_4^- during the work-up, by addition of an excess of a salt containing the chosen counter-ion, e.g. NH_4PF_6. This gives a complex that is less polar than the dichloride complex. As a result, the complex usually precipitates from the reaction mixture, hence simplifying the isolation. Bis-hexafluorophosphate complexes are usually soluble in acetone and to some extent in dichloromethane.

The electron distribution of a bipyridine coordinating to a cationic ruthenium metal centre, is different to non-coordinating bipyridines. As the metal is positively charged, it will withdraw electrons from its surroundings and thereby decrease the electron density of a coordinated bipyridine. By inductive effects, this will also affect the electron density of the ligand substituents. These effects have to be taken into account when performing reactions on ruthenium-coordinated bipyridines. As bipyridines can be rather unreactive towards substitution, coordination to ruthenium can be used to activate the heteroaromtic ring or its substituents.[22,23]

2.2　Fullerenes

The fullerene C_{60} was first discovered in 1985 during studies of the mechanisms by which carbon molecules are formed in interstellar space.[24,#] Since then there has been an tremendous development in the field of fullerene chemistry.[25,26] A property that makes fullerenes particularly interesting is the unusually high electron affinity of C_{60}, which can reversibly accept up to six electrons.[27] Many different derivatives have for this reason been used as electron acceptors in dyads. Fullerenes are also used in solid materials to

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[#] For this discovery R. F. Curl, H. W. Kroto and R. E. Smalley were awarded the Nobel Prize in chemistry in 1996.

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induce special material properties,[25,26] e.g. high-temperature superconductors.[28]

There are a range of reactions suitable for the functionalisation of fullerenes,[26,29] among them a variety of cycloadditions.[30-37] Most of these reactions occur with the double bond at the junction between two six-membered rings resulting in [6,6]-adducts. The reactivity of fullerenes is similar to that of fairly localised olefins[38] and the main driving force for addition reactions is the relief of strain in the pyramidalized sp^2-hybridized carbons atoms. In pristine C_{60} there are 30 reactive double bonds, all equivalent, and it is therefore possible to obtain polyadducts. In reality however, it is not possible to introduce more than six substituents on the fullerene core. This is due both to sterical and reactivity reasons; the reactivity decreases for each addition.[38] The hexa-adduct has its substituents spread evenly over the fullerene surface, while with lower adducts there are several possible regioisomers. With the bisadduct for example, eight different isomers exists.

Over the years, a wide variety of dyads between C_{60} and $Ru(bpy)_3$-complexes have been prepared and used for studying electron- and energy transfer processes.[26,29,39-45] A long spacer between the electron donor and acceptor increases the stability of the charge-separated state, while, on the other hand, a short spacer may favour energy transfer over electron transfer.[46]

We wanted to obtain a system with fast electron transfer, which might be achieved by using a short spacer between the ruthenium complex and the fullerene. Studies of such assemblies would give us knowledge that later also might be applied to systems where the fullerenes are replaced by single-walled carbon nanotubes. A nanotube would be able to carry the electron away from the complex and thus prevent charge recombination.

During this work we focused on three main classes of fullerene adducts; methanofullerenes, fulleropyrrolidines and fulleropyrazolines, figure 2.
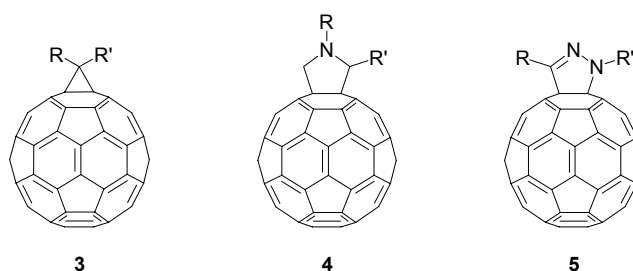

Figure 2. Schematic pictures of a methanofullerene, a fulleropyrrolidine and a fulleropyrazoline.

2.3 The Grätzel-type solar cell

One of the first reports on voltage enhancement after treatment of electrodes with a dye came in the 1880's.[47] About a hundred years later, a model was presented[48] which subsequently was developed into what now is known as the Grätzel cell.[14] The efficiency of that cell was 7.1 %.[14] Today it has been improved to approximately 10.6 % for single cells,[49] which can be compared to commercially available solar cell modules made from crystalline silicon (12-14 %) or CuInSe (CIS) (11-12 %). To increase the efficiency of the Grätzel solar cell, systems containing new combinations of semiconductors, dyes and electrolytes are needed.

The most commonly used semiconductor in Grätzel solar cells is TiO_2, since it has suitable physical properties e.g. energy levels for the valence and conducting band, it is cheap, readily available and non-toxic. TiO_2 is also used in a variety of products ranging from toothpaste to paint.

Figure 3 shows a schematic picture of a Grätzel solar cell with the semi-conductor deposited on a back-contact, covered with a monolayer of a dye that absorbs visible light, and an electrolyte.
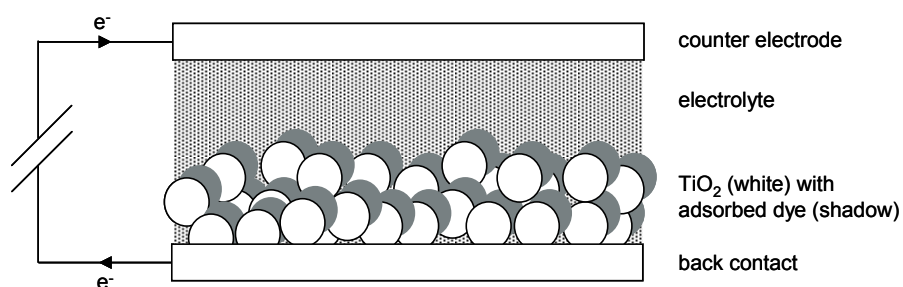

Figure 3. Schematic cross-section of a Grätzel cell.

TiO_2 has a large band gap (the difference between the valence band and the conduction band) and thus only absorbs UV light. This disadvantage can be circumvented by treating the TiO_2 with a dye that absorbs visible light. For a solar cell to be efficient, it has to absorb as much visible light as possible. One way of increasing the absorption is to have an electrode with a large surface. By using nanostructured TiO_2-particles with a diameter of roughly 20 nm, a very large surface area is obtained. Owing to the large surface of the TiO_2, a large amount of dye can attach to it, leading to a high light absorption of the cell The dye absorbs a photon and an electron gets excited and is injected into the semiconductor, figure 4. As the dye gets oxidized in that step the system has to contain an redox active electrolyte that can reduce

the dye back to its ground state. Usually the redox couple I⁻/I₃⁻ is used for this purpose. I⁻ reduces the dye upon formation of I₃⁻, which is re-oxidised at the counter electrode to close the circuit. The I⁻/I₃⁻ is usually dissolved in an organic solvent like 3-methoxypropionitrile, but also ionic liquids and different polymers can be used.[50]
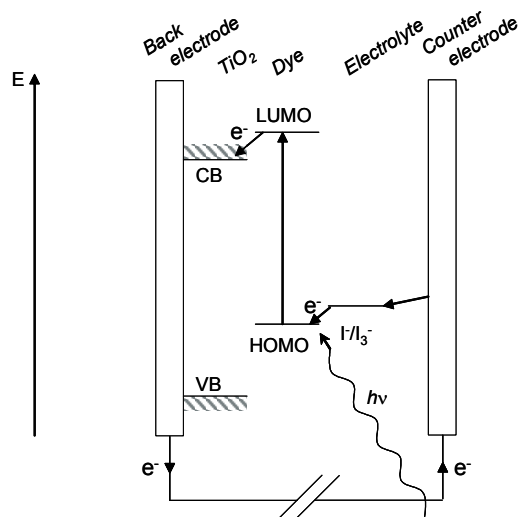

Figure 4. Schematic picture of the energy levels in a Grätzel solar cell. The energies are not scaled.

A good dye should absorb as much visible light as possible, be able to bind to the semiconductor and be able to sustain at least 10^8 cycles of oxidation and reduction. This number corresponds to about 20 years lifetime of a solar cell. Another requirement is that the LUMO of the dye should have a slightly higher energy than the conduction band of the semiconductor. When the dye absorbs energy from photons, excited electrons can be injected into the conduction band. The electrons move through the semiconductor to the outer circuit, where their energy can be used.

   Dyes for this type of solar cells are often ruthenium-based bipyridine or terpyridine complexes. At least one of the ligands should carry a linking group that binds to the semiconductor and provides a quick and efficient channel for electron injection from the excited dye into the semiconductor. Usually the linking group is a carboxyl group, but phosphonate groups have also been used.[51,52] Two dyes developed in the Grätzel group, "N3" and "the black dye", figure 5, are the most widely used.[13,53] Both have a high absorption throughout the visible spectrum and are efficient electron injectors. But still, despite the enormous amount of research in this area, the efficiency of

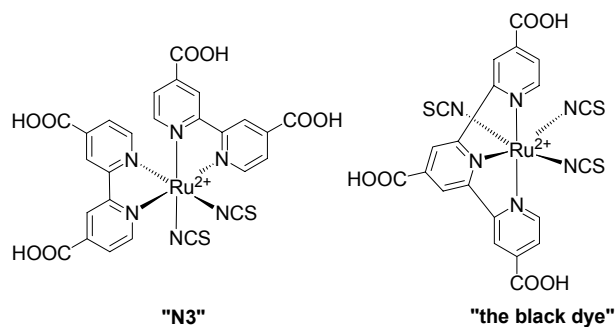Grätzel-type solar cells based on TiO_2 has not significantly increased since they were first presented.

Figure 5. Bipyridine dye "N3" and terpyridine dye "the black dye", the two most widely used dyes for Grätzel-type solar cells.
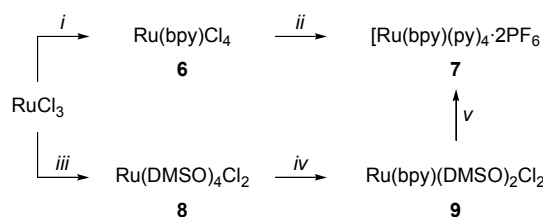
3 Mono-and bipyridine based complexes for photophysical measurements

3.1 Pyridine-based complexes [I, II]

3.1.1 Synthesis of Ru(bpy)(py)$_4$

The tris-homoleptic complex Ru(bpy)$_3$ is often used as a photosensitiser and electron donor in studies that are designed to increase the knowledge about the different processes present during electron transfer, i.e., transfer rates and mechanisms. It is therefore important to know the behaviour of Ru(bpy)$_3$. When this complex is irradiated with light, an electron on the metal is excited and transferred to one of the bipyridines. Earlier studies have shown that although Ru(bpy)$_3$ is symmetric, this charge is not evenly distributed over the three bipyridines as might be expected, but instead it is localised on one of them.[16,54,55] There are some different theories about how and when this localisation occurs,[16,55,56] and time-resolved absorption experiments have been carried out, which gave different results and interpretations.[57-61] In order to get more information about these processes, we conducted a new study of Ru(bpy)$_3$, using Ru(bpy)(py)$_4$, **7** (scheme 2) as a reference. As **7** only contains one bipyridine, and pyridines have a too high reduction potential to accept the extra electron, the charge will be localised on the bipyridine without any possibility to move. Differences in the results from Ru(bpy)$_3$ and **7** can therefore be interpreted as a delocalisation of the electron over more than one bipyridine.

To prepare **7**, a new method was developed. The previously published route, from RuCl$_3$ *via* Ru(bpy)Cl$_4$, **6**, scheme 2, is very time consuming with a reaction time of three weeks for the first step.[62] To circumvent this time consuming step, complex **7** was instead prepared *via* Ru^{II}(DMSO)$_4$Cl$_2$, **8**, which is obtained in the reduction of Ru^{III}Cl$_3$ in refluxing DMSO. To fulfil the preferred hexa-coordination around the metal, DMSO acts as ligand. This is a useful starting material in the preparation of heteroleptic complexes, as the metal has already been reduced and only the coordination of the ligand needs to be done. This approach is especially useful if the ligand is sensitive towards reductions.

Scheme with:
RuCl$_3$ →(i) Ru(bpy)Cl$_4$ **6** →(ii) [Ru(bpy)(py)$_4$·2PF$_6$ **7**
RuCl$_3$ →(iii) Ru(DMSO)$_4$Cl$_2$ **8** →(iv) Ru(bpy)(DMSO)$_2$Cl$_2$ **9** →(v) **7**

Reagents and conditions: i) 2,2´-bipyridine, 1M HCl (aq.), r.t., 3 weeks (24 %); ii) pyridine, EtOH:H$_2$O 3:1, 22 h, then NH$_4$PF$_6$; iii) DMSO, reflux, 30 min (46 %); iv) 2,2´-bipyridine, CHCl$_3$, reflux, 1 h; v) pyridine, EtOH, reflux, 19 h (32 %).

Scheme 2. Two alternative routes to prepare complex **7**.

Complex **8** was treated with one equivalent of 2,2´-bipyridine to obtain **9**, which in turn was refluxed in a pyridine containing solution yielding the target complex **7**. Due to the presence of four monodentate ligands, **7** is not very stable which made removal of decomposition products slightly problematic. However, the exchange of pyridines for solvent molecules did not affect the electron transfer study, as the important part was to have a complex with a single bipyridine ligand surrounded by ligands with higher reduction potentials. The new pathway towards complex **7** is much faster than the previously published method; **7** can be obtained within two days instead of several weeks.

3.1.2 Synthesis of Ru(bpy)$_2$(4-X-py)$_2$ (X = SH, COOH)

TiO$_2$ is the most commonly used semiconductor in Grätzel solar cells but ZnO could be an interesting alternative, as it has properties very similar to TiO$_2$ such as the energies for conduction- and valence bands. For a ruthenium-bipyridine complex to be useful in a Gräzel cell, suitable attachment units have to be present. As mentioned in chapter 2, these units are usually carboxyl or phosphonate groups. Dyes used for TiO$_2$ can to some extent be used with ZnO,[63-65] but problems with desorption from the oxide surface and dye aggregation have been observed.[66] Finding other linking groups, more suitable for ZnO, could be a way to circumvent the problems with the unstable connection between the dye and the oxide surface. A preliminary study of small azo dyes was made by H. Wolpher in order to find new potential linking groups for use on ZnO.[67] In that work, ZnO electrodes were soaked in solutions containing diazadiphenyls substituted with different functional groups. For most of the investigated linkers, rinsing the electrodes with solvent was sufficient to remove the azo-dye from the electrode. Except for carboxylic acids, only thiol containing dyes gave a permanent colouring of

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the ZnO electrodes. No photoelectrochemical measurements were made in that study, it only showed that thiols interacted with the ZnO-surface, but not if they would mediate electron injection into the semiconductor. To be able to obtain such information, a ruthenium-bipyridine complex including thiol groups was prepared. For this preliminary study, commercially available 4-thiopyridine was used as ligand to form complex **10**, scheme 3.
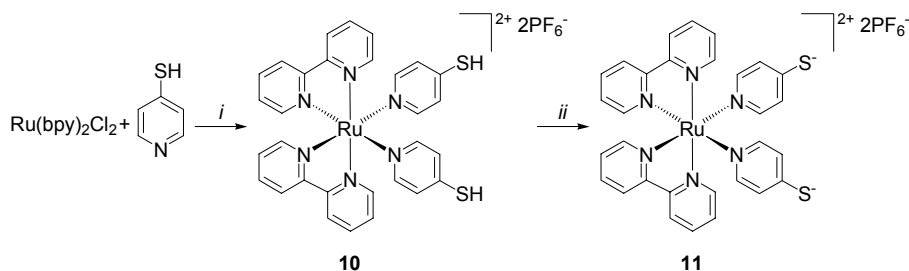
Reagents and conditions: i) ethanol, reflux, 23 h, then NH_4PF_6 (83 %); ii) filtration through neutral Al_2O_3.

Scheme 3. Preparation of dithiol complexes **10** and **11**.

The dithiol complex **10** was obtained by refluxing 4-thiopyridine and $Ru(bpy)_2Cl_2$, scheme 3. It was noticed that the yields were higher if ethanol or ethanol:water was used as solvent instead of 2-methoxyethanol (>80 % and 25 % respectively). Sometimes the higher boiling point and the lower polarity of 2-methoxyethanol can be a benefit but in this case those properties made the complex more difficult to isolate.

In the purification of **10**, the crude complex was filtered through neutral Al_2O_3, during which the colour of the complex changed from wine red to greyish blue. This colour change could be caused by deprotonation of the thiols and/or formation of a cluster containing an aluminium species. Attempts to form crystals suitable for X-ray crystallography of this complex, **11**, failed. The presence of aluminium in **11** was later ruled out by atom absorption measurements.[‡] However, as the titration of **10** with NaOH, figure 6, resulted in a similar colour change as for **11**, deprotonation of the thiols was the most likely explanation. But as the agreement is not perfect between the UV-vis absorption spectra recorded for **11** and the deprotonated **10**, other actions can not be ruled out. As the difference in colour was so distinct, **11** was treated as a separate substance in the forthcoming solar cell evaluation.

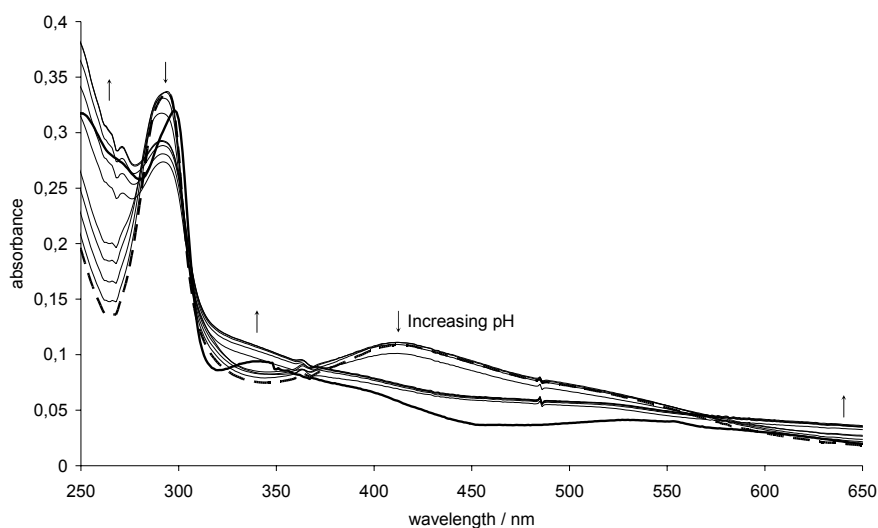[‡] made by Dr Jean Pettersson, Department of Chemistry, Analytical Chemistry, Uppsala University

Figure 6. UV-vis spectra obtained during titration (~ pH 2–9) of a methanolic solution of **10** with aq. NaOH. The dashed line represents the spectra recorded before addition of NaOH and the thick solid line the absorption spectra for **11** (filtered trough Al_2O_3).

By using carboxylic acid complexes **12** and **13** as references it was possible to see whether features from **10** arose from the sulphur linking group or from the presence of two pyridines instead of one bipyridine. These complexes were prepared in the same way as the thiol complex **10**, i.e., by refluxing $Ru(bpy)_2Cl_2$ and the selected ligand in ethanol, figure 7.
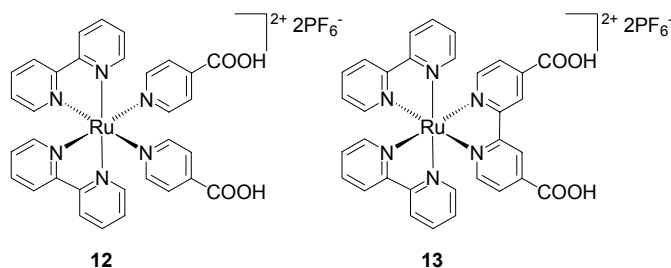

Figure 7. Two complexes used as references in the evaluation of thiols as linking groups between dye and metal oxide surface.

3.1.3 Preparation of simple Grätzel-type solar cells

To investigate whether the thiol complexes **10** and **11** were capable of injecting electrons into ZnO, simple solar cells were prepared from dye treated

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ZnO electrodes, a counter electrode and an electrolyte. ZnO electrodes were prepared by placing a paste of ZnO in water:acetylacetone on a sheet of conducting glass, and spreading it with a glass-rod to a thin film. A piece of adhesive tape served as spacer to ensure an even ZnO film of the right thickness (about 10 μm). To increase the contact between the oxide particles, the electrodes were sintered at 380 ºC for 30 minutes. The ZnO electrodes were placed in 0.5 mM ethanolic solutions of **10**, **11**, **12** and **13** for 30 min, 1 h, 2.5 h, 6 h, 14 h and 25 h, three electrodes for each dye and time, before they were rinsed with ethanol to remove excess dye and then air-dried. Different sensitising times were used to investigate whether this factor would affect the efficiency of the cell. Such a dependence has been reported for carboxylic acid dyes on ZnO.[66]

The dye-treated electrodes were placed together with a platinum covered SnO_2 counter electrode. To prevent short-circuiting of the cell, the two electrodes should not be in direct contact but be separated by some electrolyte. In order to decrease the risk of this, a small piece of tissue paper was used as spacer between the electrodes. The electrolyte could then be immersed between the electrodes by capillary forces.

3.1.4 Photophysical measurements

A simple way to evaluate the efficiency of a solar cell is to determine the IPCE, the amount of electrons withdrawn from the cell divided by the number of photons of a certain energy hitting the cell. Another method is by illuminating the cell with white light, i.e. all wavelengths of the visible spectrum, and determine the photo-induced current in a resistance-free (short-circuited) cell, I_{sc}, and the voltage in a cell with infinite resistance (open circuit), V_{oc}. In a simplified view, higher values of these parameters mean a better cell.

Large differences between the individual electrodes, though treated in the same way, were observed, figure 8, and no clear conclusion of any sensitising-time dependence could be drawn. For **11**, the trend seemed to be that the efficiency increased to a maximum after 14 hours and then decreased again. With **12** it appears that the efficiency was unaffected by the sensitising time in contrast to the results of Keis *et al.* which claim a time-dependence for a similar carboxylic acid dye.[66]
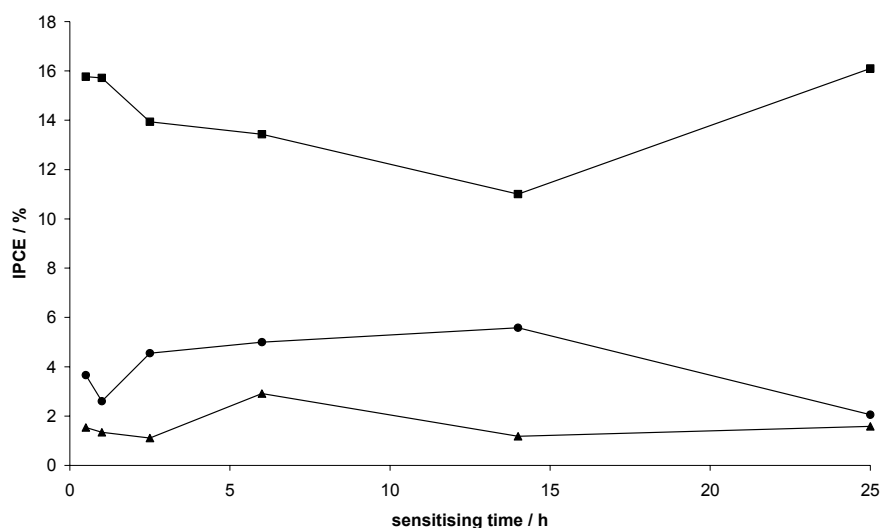
Figure 8. The effect of sensitising time on the $IPCE_{max}$ at 460 nm for **10** (▲), at 500 nm for **11** (●)and at 440 nm for **12** (■). The mean values are shown.

The highest IPCE, I_{sc} and V_{oc} values for **10**, **11** and **12** are summarised in table 1. When comparing the results from the measurements, a general observation was that the best results from the pyridine containing complexes, were obtained with the carboxylic acid dye **12**.

Table 1. Photoelectrochemical properties for ZnO electrodes treated with solutions of **10**, **12** and **12**. The uncertainty intervals are calculated for 95 % confidence. For each dye and sensitising time, three electrodes were evaluated.

Complex	$IPCE_{max}$	I_{sc}	V_{oc}	sensitising time
	(%)	(mA / cm^2)	(mV)	(h)
10	2.9 ± 1.6^a	0.036 ± 0.026	19 ± 14	6
11	5.6 ± 2.2^b	0.045 ± 0.004	32.1 ± 3.3	14
12	16.10 ± 0.97^c	0.166 ± 0.010	168.7 ± 4.6	25

[a]At 460 nm, [b]at 500 nm, [c]at 440 nm

An unexpected feature was that **11** gave higher efficiencies than **10**. The extinction coefficient (at 297 nm) of **11** ($3.7 \cdot 10^4$ cm^{-1}M^{-1}) in solution is higher than that of **10** ($1.8 \cdot 10^4$ cm^{-1}M^{-1}). The colour intensity of the electrodes treated with **11** were, however, much lower than the electrodes treated with **10**. This means that less **11** was adsorbed on the ZnO surface. The higher efficiencies recorded with **11** might be an indication of a higher electron injecting ability of **11** than of **10**. Depending on the number of protons

20

present in the dye, the electronic properties of the semiconductor are affected and thereby influencing both the adsorption behaviour of the complex to the oxide surface and the electron injection ability.[68]

When comparing the pyridine containing complexes **10** and **12** with **13**, the bipyridine analogue of **12**, it is clear that **13** gives the best results of this study. The IPCE$_{max}$ for **13** is ~23 %, which is much higher than for **10** (2.9 %) and **11** (5.6 %) and slightly higher than for **12** (16.1 %). The reason for this is that the linking groups in **10**, **11** and **12** are sitting on pyridines. The reduction potentials for pyridines are generally higher than for bipyridines, which leads to transfer of the excited electron to the bipyridines present in the complex instead of to the pyridine, from where it can be injected into the metal oxide.

3.2 Bipyridine-based complexes [(V)]

The photophysical evaluation of Ru(bpy)$_2$(pySH)$_2$, **10**, showed that the sulphur link was able to mediate electron injection into ZnO, but as complexes where the linking group is sitting on a bipyridine give higher efficiencies and are more stable than those that contain monopyridines, a complex such as **15**, including 4,4´-dithio-2,2´-bipyridine, **14**, figure 9, probably would be a better dye than **10** or **11**.
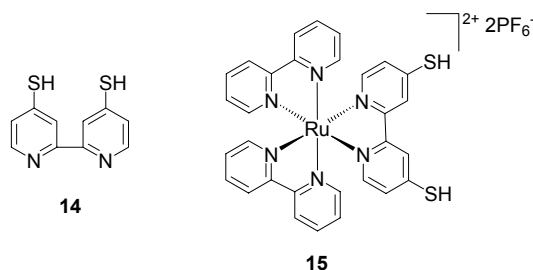

Figure 9. The thiol-containing target molecules.

One route to prepare dithiobipyridine **14** could be *via* a substitution reaction on dichlorobipyridine **18**, scheme 4, which in turn can be obtained from bipyridine in three steps. The same approach is used to obtain the monosubstituted analogues, which will also be discussed here.

Bipyridines are rather unreactive towards substitution reactions but can be activated by *N*-oxidation. This activates the pyridine ring towards both electrophilic and nucleophilic attack in the 2- and 4- positions.

To obtain the dioxide **16** in good yield (~ 90 %) the bipyridine was heated in a mixture of H_2O_2 and acetic acid.[69] Upon addition of acetone to the reaction mixture, the pure product precipitates. If instead the monooxide **19** is desired, only one molar equivalent of the oxidizing agent should be used. In that case, mCPBA is preferred over H_2O_2[70] as it allows better control of the amount of oxidant present in the reaction mixture.
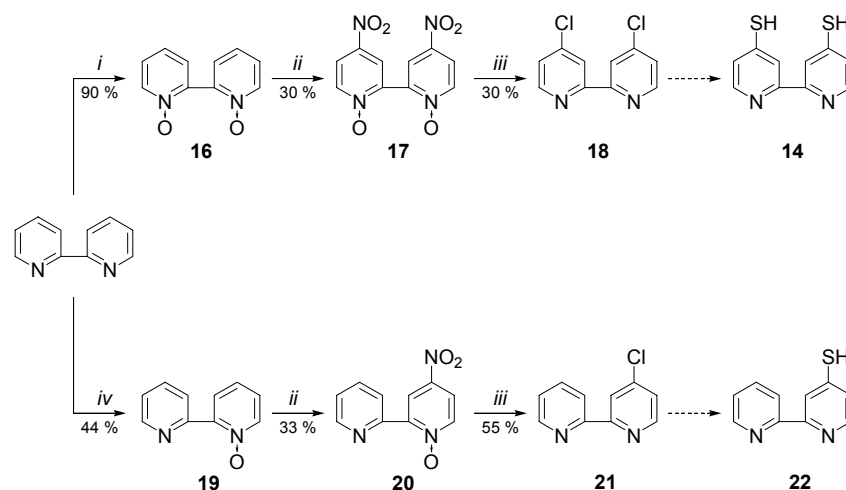
Reagents and conditions: i) H_2O_2 (35 % in water), AcOH, 80 °C, 7 h, ii) H_2SO_4 (25 % oleum), HNO_3 (fuming), 100 °C, 4 h, iii) AcCl, 60 °C, 15 h then PCl_3, 65 °C, 2 h, iv) mCPBA, CH_2Cl_2, r.t., 22 h.

Scheme 4. Di- and monosubstitutions on 2,2´-bipyridine.

Nitrations of aromatic rings can be performed using a variety of reagents, the most common of which is a mixture of sulphuric acid and nitric acid. The higher concentration of the acids, the stronger reagent. Sometimes fuming sulphuric and nitric acid are required to promote the reaction. The choice of acid combination can be crucial for the outcome of the reaction depending on how acid-sensitive or unreactive the reactant in question is. In the case of bipyridine, rather harsh conditions were required to obtain the desired product. When using concentrated HNO_3 and concentrated H_2SO_4 with dioxide **16**, the mononitrated product **20** was obtained in 26 % instead of the desired dinitrobipyridine **17**. If the sulphuric acid was saturated with SO_3, some of the starting material was destroyed, probably due to polymerization induced by the strong acid. Product mixtures were obtained both when using the saturated sulphuric acid with concentrated nitric acid and with fuming nitric acid. In the latter case, however, there seemed to be a slightly larger amount of desired product. One difficulty with **17** is its low solubility in most sol-

vents, only in DMSO is the solubility satisfactory. This makes purification slightly troublesome and it is desirable to obtain the pure product directly from the reaction. By diluting the SO_3-saturated sulphuric acid slightly, so it contained 25 % SO_3,[69] the 4,4´-nitrated product **17** could be isolated in 30 % yield by filtration of the reaction mixture after addition of water.

To obtain the mono-nitrated product **20** from **19**, less harsh conditions were required for the reaction, by using KNO_3 in concentrated H_2SO_4 [70] the yields were about 30 %. Slightly better yield (~ 40 %) was obtained if the same conditions as for **17** were used, i.e. fuming HNO_3 together with sulphuric acid containing 25 % oleum. The chlorides **18** and **21** were prepared by using acetyl chloride to substitute the nitro groups subsequently followed by reduction of the *N*-oxides using PCl_3.[71]

In order to prepare the dithiobipyridine **14**, some different methods were tried. One of them was the reaction between pyridyl halides and benzylthiol or ethylthiol.[72] However, as the results were not optimal with rather low yields and mixtures of the desired thiol and thioethers, together with the olfactorial unpleasantness of the thiols, this route was not developed further.

Another route tried was by carry out the substitution on complexed chlorobipyridine. With 2- and 4-thiopyridines there is an equilibrium between thiol and thione tautomers, scheme 5. Experiments and calculations made on 2- and 4-thiopyridine show that the equilibrium is usually shifted towards the thione, but that solvent and concentration both play important roles.[73-78] According to Anderson *et al.*, reacting **18** with Na_2S in basic conditions followed by acidification yields the thione **23** as a solid with low solubility.[69] Besides the reported low solubility, obtaining the thione means that the electron pairs on the nitrogens would be occupied by protons, which could affect the complex formation.
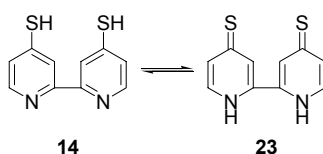
Scheme 5. Tautomerisation of dithiol **14**.

To fully avoid the thiol–thione tautomerism, the order of the last two steps in the reaction sequence was reversed. Prior to substitution of the chlorides to thiols, **18** was coordinated to ruthenium to form complex **24**, scheme 6. The nitrogens are now unavailable for protonation, but, as mentioned in chapter 2.1, it also serves as an activation of the bipyridine towards nucleophilic substitution as the metal makes the rings more electron deficient.
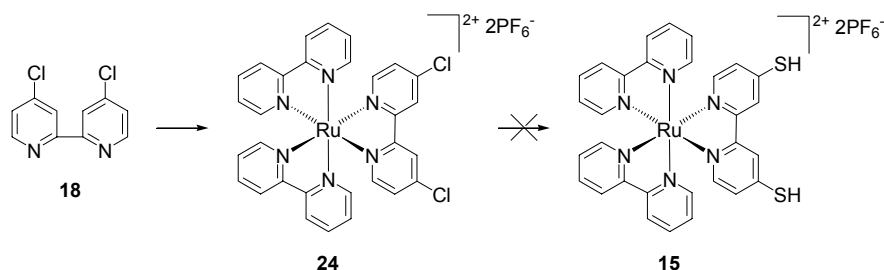
Reagents and conditions: i) Ru(bpy)$_2$Cl$_2$, EtOH, reflux, 15 h, then NH$_4$PF$_6$ (89 %); ii) Na$_2$S, DMF, reflux, 1.5 h (no product isolated).

Scheme 6. Substitution on coordinated dichlorobipyridine.

When complex **24** was treated with Na$_2$S in different solvents such as DMF, THF and acetone:water, mixtures of substituted complexes were obtained. ^{1}H NMR studies revealed groups of overlapping multiplets in the aromatic region and from mass spectrometry, fragments originating from disulphides, thioethers and chlorine-containing bipyridines could be found. As the different products were not possible to isolate, no further identification was attempted.

Since the preparation of the thiolated bipyridine **14** and its ruthenium complex **15** involved several different problems, the project was put on hold. Recently, the preparation of **15** was presented by Hansen *et al.* who reacted **24** and NaSH in THF in a sealed tube at 115 ºC for 9 hours and obtained **15** in more than 85 % yield.[79] Similar results could likely be obtained using, for example, microwave heating.

4 Synthesis of fullerene adducts

4.1 Approaches towards fullerene-containing dyads

There are many different ways to obtain dyads containing ruthenium-bipyridine complexes and C_{60}. Starting from bipyridine, the first step can either be formation of a suitably substituted fullerene adduct followed by complexation, upper route in scheme 7, or performing the coordination to the ruthenium prior to the addition of C_{60}, lower route. Both alternatives have their advantages and disadvantages. The presence of a C_{60}-moiety can sometimes increase the instability and sensitivity of a compound. By not introducing the fullerene until in the last step problems concerning instability can be decreased. On the other hand, a range of byproducts such as polyadducts are usually formed in addition reactions to C_{60}, which usually can be removed by flash chromatography. The presence of the doubly charged complex can, however, make purification problematic and hence lower the overall yield of the dyad.
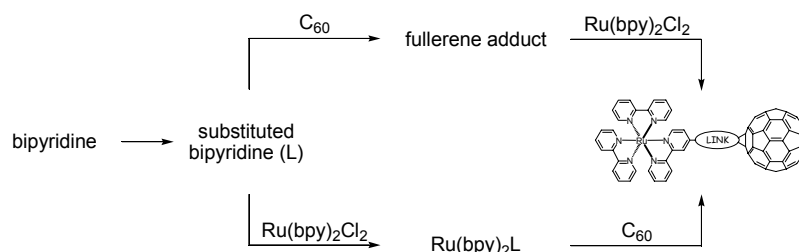
Scheme 7. Two different approaches to obtain a $Ru(bpy)_n$-C_{60} dyad.

The metal also decreases the electron density on the bipyridines, which can lead to changed chemical properties of the substituents. As most additions to C_{60} are nucleophilic, e.g. dipolar cycloadditions, this can make addition to the fullerene difficult or impossible. A third issue regards the choice of solvent. Reactions involving C_{60} are preferably performed in toluene to ensure that the fullerene is completely dissolved and thus decreasing the risk of obtaining polyadducts, but $Ru(bpy)_n$ complexes are usually only soluble in more polar solvents such as acetone. Also by using the other alternative,

fullerene addition first and coordination in the last step, similar problems can arise. $Ru(bpy)_2Cl_2$ is soluble in water and ethanol, whereas the fullerene adducts usually are much less polar. For both approaches towards $Ru(bpy)_n$-C_{60} dyads, a main task is to find suitable solvents and this issue, among others, will be discussed in the following chapter.

## 4.2 Synthesis of methanofullerenes [(V)]

4.2.1 General

One of the first reactions developed for the functionalisation of fullerenes was reported by Bingel in 1993.[30,32] An *in situ* generated carbene reacts with a double bond in C_{60}, often called the Bingel- or the Bingel-Hirsch cyclopropanation, scheme 8, forming adducts called methanofullerenes. To favour the carbene formation, both R and R' should be electron withdrawing. In the first report,[30] diethyl chloromalonate was used, but it was later noted that the yields were higher if diethylmalonate was used in the presence of CBr_4 or I_2.[32] It is also possible to generate the carbene from diazo compounds.[80]
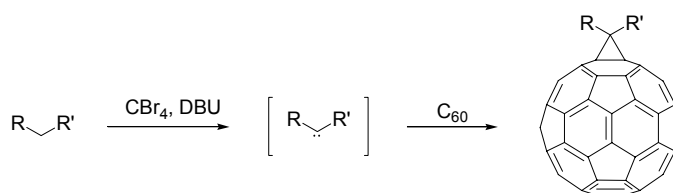
Scheme 8. The Bingel-Hirsch cyclopropanation.

4.2.2 Preparation of fullerene adducts

Carboxyl groups are useful functional groups for further substitutions, and as diethylmalonate is a readily available starting material, product **25** was prepared *via* the Bingel-Hirsch cyclopropanation, scheme 9. This was made by reacting diethylmalonate and C_{60} with DBU and CBr_4 in toluene. The thus formed cyclopropanated diester was hydrolysed to yield **26**.
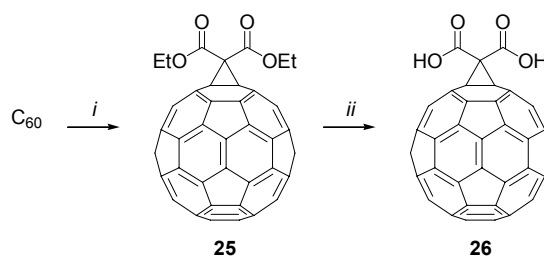
Scheme 9. Preparation of fulleromalonic acid **26**.

Two methods for hydrolysis were tested; aqueous NaOH in THF[81] and NaH in toluene with methanol as a co-reagent in a second step.[82] When a solution of **25** and NaH in dry toluene was stirred overnight, a dark violet solution was obtained. The colour disappeared when methanol was added and the disodium salt of **26** was formed as a brown precipitate. The reaction with NaH is considered to be a hydrogenolysis of the O–Et bond but could also be an hydrolysis by traces of water in the methanol.[82,83] To test the latter hypothesis, a small amount of water was added at the same time as the NaH. This resulted in an immediate formation of a dark brown precipitate, but only a small amount of product could be isolated. The hydrogenolysis is therefore a more likely mechanism. The method involving NaOH took longer time and gave lower yields than the NaH-method. A drawback with both methods is the rather tedious work-up as usually centrifugation of large volumes of suspensions was involved.

4.2.3   Towards methanofullerene-Ru(bpy)$_n$ dyads

Several routes to Ru(bpy)$_n$-methanofullerene dyads can be envisaged, of which formation of an amide link by using activated fulleromalonic acid **26** and reacting it with, for example, 4-aminobipyridine to obtain the amide-bridged dyad **30**, scheme 10, seemed an obvious first choise. As mentioned earlier, it can sometimes be beneficial if the C$_{60}$ moiety is introduced as late as possible in the reaction sequence. 4-Aminobipyridine, **27**, should therefore be coordinated to ruthenium to yield **28** before being reacted with the *N*-hydroxysuccinimidyl ester **29**, scheme 10. According to Lampart *et al.*, the carboxylic acids can be activated by preparing **29** from the fulleromalonic acid **26**.[83] Compound **29** is an important intermediate as it not only promotes

the amide coupling, but also because one of the carboxylic acid groups in **26** is removed in the reaction.

The activated ester, **29**, was prepared by reacting **26** with three equivalents each of DCC and *N*-hydroxysuccinimide in THF. The best result from this reaction so far has only been 13 % yield. According to Lampart *et al.* the synthesis of **29** is very sensitive to the proportions of *N*-hydroxysuccinimide and DCC.[83]
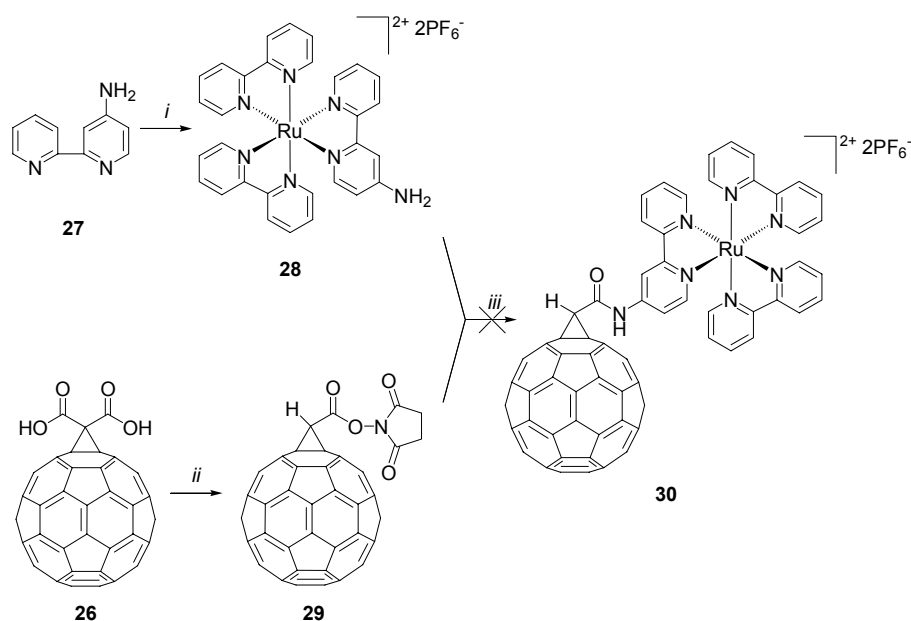
Reagents and conditions: i) Ru(bpy)$_2$Cl$_2$, EtOH, reflux, 6 h, then NH$_4$PF$_6$ (74 %), ii) N-hydroxysuccinimide, DCC, THF, r.t., 2 days (0-13 %) iii) CH$_2$Cl$_2$, r.t., 22 h (no product formed).

Scheme 10. Route towards amide containing dyad **30**

In the reaction between **29** and **28**, scheme 10, no product was obtained, which might be because the complexation made the amino group too electron deficient and therefore less reactive towards the ester. It could have been better to use the free amine **27** instead.

In combination with the low yields obtained in the reactions relating to the preparation of the dyad **30** and the fact that the fullerene has to be introduced very early in the reaction sequence, we decided to focus our efforts on other methods of obtaining fullerene adducts.

4.3   Cycloadditions of 1,3-dipolar compounds [III, IV]

4.3.1   General

Among the methods for preparing substituted fullerenes, 1,3-dipolar cycloadditions have become one of the most useful tools as a range of different heterocyclic five-membered rings can be annulated to the fullerene cage, containing almost any groups. This chapter will discuss the formation and further use of the products from 1,3-dipolar cycloadditions using azomethine ylides and nitrile imines as dipolar reagents, yielding fulleropyrrolidines and –pyrazolines respectively. Fulleropyrrolidines are among the most widely used fullerene derivatives whereas the fulleropyrazolines are more uncommon.

Azomethine ylides were prepared *in situ* from an aldehyde and a glycine derivative, scheme 11,[35,84,85] There are several other methods, e.g. pyrolysis of aziridines, desilylation of α-trialkylsilylonium salts and deprotonation of amine *N*-oxides to obtain this type of dipolar compounds,[86,87] however not explored here.
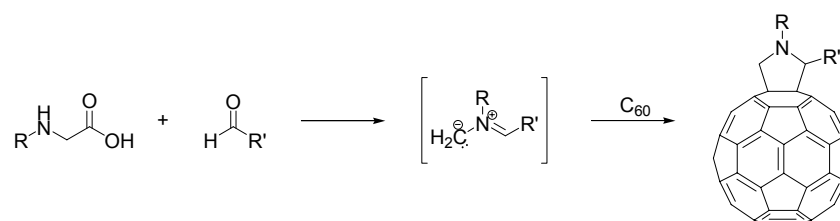
Scheme 11. General formation of fulleropyrrolidines.

There are two possible ways to connect a bipyridine *via* a pyrrolidine unit; either *via* the nitrogen (as R in scheme 11) by using a bipyridine substituted glycine derivative, or *via* carbon if an aldehyde substituted bipyridine (R' in scheme 11) is used.

Fulleropyrazolines can be obtained by the 1,3-dipolar cycloaddition of a nitrile imine to C_{60}, scheme 12, a reaction similar to the fulleropyrrolidine formation. The nitrile imine was formed *in situ* in two steps using NBS or NCS and base. In this case the pyridine/bipyridine was *C*-connected
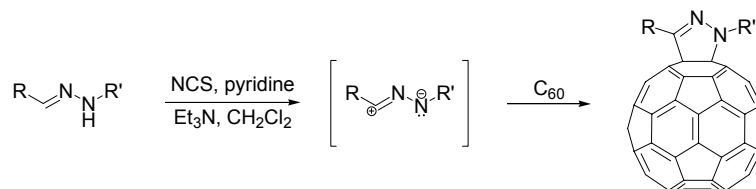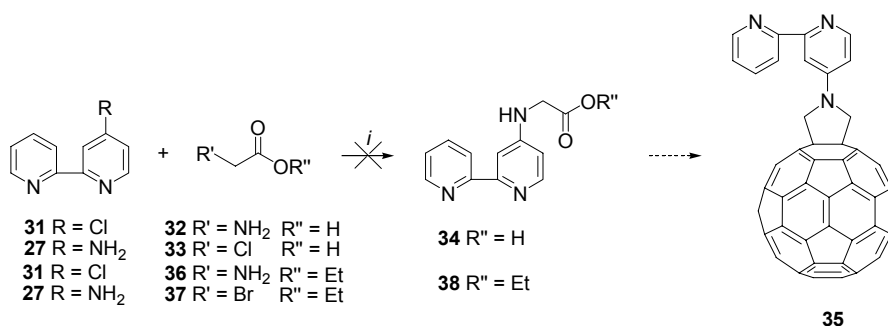

Scheme 12. General formation of a fulleropyrazoline.

29

4.3.2 Fulleropyrrolidines

Towards N-substituted fulleropyrrolidines

A key intermediate in the synthesis of the *N*-substituted fulleropyrrolidine **35**, is the glycine derivative **34**, scheme 13. This should be possible to prepare either from the chlorobipyridine **31** or with **27** as nucleophile. Due to the zwitterionic properties typical for amino acids and acid/base behavior of the starting materials, the work-up proved difficult. As a result, no product could be isolated from the starting materials and NMR studies could therefore not confirm any formation of **34**.


31 R = Cl	**32** R' = NH$_2$ R" = H	**34** R" = H
27 R = NH$_2$	**33** R' = Cl R" = H	
31 R = Cl	**36** R' = NH$_2$ R" = Et	**38** R" = Et
27 R = NH$_2$	**37** R' = Br R" = Et	

Reagents and conditions: i) Na$_2$CO$_3$, CH$_2$Cl$_2$, r.t., 19 h (products not isolated).

Scheme 13. Route to *N*-pyrrolidylbipyridine **35**.

To avoid the zwitterionic intermediate, the ethyl ester of the acid was used instead. However, this did not improve matters, and no products were obtained. In the case of **27** this is probably due to the too low nucleophilicity of the amino group, as the pyridine ring tends to make substituents slightly electron deficient. The generally low reactivity of bipyridines towards nucleophilic aromatic substitutions is probably responsible for the lack of reaction between **31** and **36** under the conditions used.

In a slightly different approach to obtain a bipyridine substituted glycine derivative, a reductive elimination between ethylglycinate and bipyridine carboxaldehyde was performed, scheme 14. The aldehyde-substituted bipyridine was obtained from dimethyl bipyridine in a selective monooxidation of using SeO$_2$. The yield is usually rather low, 30-40 % (reaction in dioxane gives slightly better yields than in diglyme).
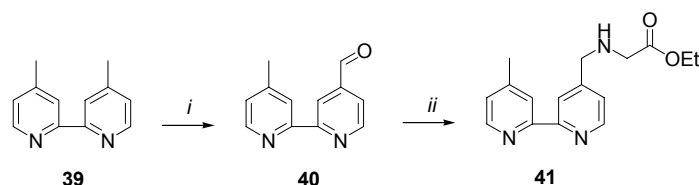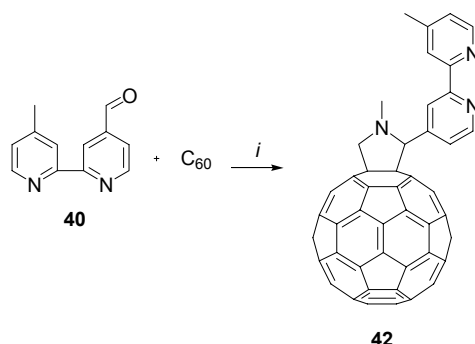
Reagents and conditions: i) SeO$_2$, 1,4-dioxane, reflux, 17 h. (14-39 %); ii) glycine ethyl ester, AcOH, EtOH, MW 120 °C, 25 min, then NaBH$_3$CN, MW 120 °C 5 min (80 %)

Scheme 14. Route to bipyridine glycine derivative **41**.

A reductive amination between **40** and ethylglycinate was performed using NaBH$_4$CN and a catalytic amount acetic acid in alcoholic solvent. The imine was allowed to form for 1 hour at room temperature before addition of the reducing agent. After 20 hours at room temperature, all the aldehyde was consumed. The isolated product was, however, not the desired **41**, but the bipyridine alcohol. When reacting the aldehyde and the amine using micro-wave heating there was still aldehyde left in the solution after 10 minutes (120 °C) but all aldehyde had been converted to the imine after an additional 15 minutes. Addition of NaBH$_4$CN to this solution yielded **41** after another 5 minutes in the microwave reactor. This bipyridine derivative has not yet been evaluated in reaction with C$_{60}$.

C-substituted fulleropyrrolidines

In order to obtain a *C*-substituted fulleropyrrolidine, bipyridine carboxalde-hyde **40** was refluxed in toluene together with C$_{60}$ and *N*-methylglycine, scheme 15. In this reaction it is necessary to have a five-fold excess of the aldehyde,[84] but by extracting the reaction mixture with Na$_2$S$_2$O$_5$ after the reaction it turned out to be possible to recover ~ 30 % of the aldehyde. This removal of unreacted starting material also simplifies purification of the product **42**. Fullerene adducts are usually possible to purify by flash chroma-tography using a toluene-containing eluent. With pure toluene, unreacted C$_{60}$ moves with the front on silica and can thus be recovered. The adducts can then be eluted by continued use of only toluene or by adding a certain amount of a second solvent. In the case of purifying **42**, it happend to have the same retention on silica as **40** in all solvent mixtures tried, and the re-moval of the aldehyde prior to chromatography was thus crucial to isolate pure **42**.

Reagents and conditions: i) N-methyl glycine, toluene, reflux, 21 h (0-18 %).

Scheme 15. Formation of fulleropyrrolidine **42**

4.3.3   Fulleropyrazolines

Fulleropyrazolines can be obtained from a reaction where a hydrazone is transformed into a nitrile imine that adds to one of the double bonds in the fullerene. Our objective was to prepare two different fullerene adducts, one containing a bipyridine moiety and one containing a pyridine connected to the pyrazoline in 2-position. The latter product might be able to form a ruthenium containing dyad with the metal coordinating to the pyridine and the double-bonded pyrazoline nitrogen. This would result in a tight dyad with the metal sitting very close to the fullerene moiety and possibly interesting photophysical and -electrochemical properties.

The hydrazones in this work were obtained by reacting 4-formylpyridine or -bipyridine and an arylhydrazine, scheme 16. Both hydrazones containing a phenyl- or 2,4-dinitrophenyl group were used to elucidate whether this would result in any differences in reactivity of the cycloaddition. The presence of the electron withdrawing nitro groups could also affect the electron transfer in the target fullerene–Ru(bpy)$_n$ dyads.
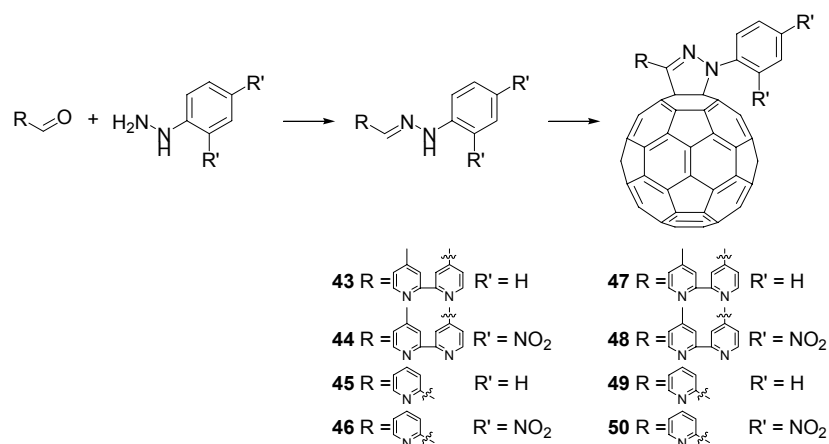
Scheme 16. Hydrazones and fulleropyrazolines synthesised.

43 R = ... R' = H   **47** R = ... R' = H

44 R = ... R' = NO$_2$ **48** R = ... R' = NO$_2$

45 R = ... R' = H   **49** R = ... R' = H

46 R = ... R' = NO$_2$ **50** R = ... R' = NO$_2$

Preparations of the hydrazones **43-46** by refluxing the aldehydes and hydrazines in ethanol went smoothly, regardless of hydrazine substituents. The products precipitated reasonable pure from the reaction mixture. As **43** displayed a strong pH-dependence both regarding the colour of the product and the appearance of the NMR spectrum, the identification was difficult. These effects were not as pronounced for hydrazones **44**, **45** and **46**.

In a published procedure regarding addition of 1,3-dipolar reagents to C$_{60}$, yielding fulleropyrazoline derivatives, the reactions were performed in CH$_2$Cl$_2$.[37] As the solubility of C$_{60}$ in dichloromethane is only 0.26 mg/ml,[88] the C$_{60}$ might not be properly dissolved unless a large volume of solvent is used. That would lead to an excess of the dipolar reagent in the solution and increased risk of polyaddition. A better choice of solvent, regarding the fullerene, would be for example toluene, or maybe even better, substituted naphthalenes.[88]

An important issue to take into account when performing additions to fullerenes is the presence of several equivalent double bonds and thereby the risk of obtaining polyadducts. If only looking at the bisadducts, a mixture of addition patterns can usually be seen. The distribution between these follows to a large extent the probability of forming a certain adduct as there, for some of them, are several double bonds available resulting in the same adduct. If the substituents are large, then steric factors will dominate the addition pattern.[89-91]

In this work, the effect the use of toluene would have on the outcome of pyrazoline formation was studied. By dissolving the fullerene in toluene before the nitrile imine is added the risk of polyaddition ought to be decreased. The formation of nitrile imines is easier in CH$_2$Cl$_2$ as the hydra-

zones are more soluble in polar solvents, but if such a solution is added to a toluene solution of C_{60} the fullerene precipitated. When the pyrazoline formation was carried out as a one-pot reaction, using dichloromethane as solvent, several by-products were obtained. In order to avoid these unwanted reactions, some attempts were made to use NCS instead of NBS as the former would, for example, be less prone to react with the fullerene double bonds. However, this resulted in a lower yield of the desired cycloaddition product and a certain amount of by-products. Reactions using the dinitrophenyl-containing hydrazones **44** and **46** did not result in any fullerene adducts, when using NBS as halogen source. The fulleropyrazoline **50** could however be obtained using NCS instead.

A common feature for the fulleropyrazolines **47-50** is that they are problematic to isolate. After addition reactions to C_{60}, more often than not there remains some unreacted C_{60} in the reaction mixture. This can generally be removed and recovered by flash chromatography using silica and toluene since C_{60} moves with the front. The fulleropyrazolines have, however, similar retentions as pristine C_{60}, therefore, rather long columns are required. Moreover, for the bipyridine-containing fulleropyrazolines **47** and **48**, a second column is required to separate the monoadduct from the different bisadducts.

As the solubility of the hydrazones in this work is rather low in toluene, the formation of the hydrazonyl bromide would be facilitated by longer reaction times and higher reaction temperature. It is also advantageous to do this reaction separate from C_{60} to avoid any reaction between the fullerene and the NBS. These factors will be taken into account in the future work.

4.3.4 Complexation of fullerene ligands

As described in chapter 2.1, $Ru(bpy)_2(\eta^2\text{-}L)$ complexes are usually prepared by refluxing the chosen ligand and $Ru(bpy)_2Cl_2$ in a polar solvent, like ethanol, followed by addition of a PF_6^--containing salt. The exchange of counter ion from Cl^- to PF_6^- usually makes the complex less polar. When using the fullerene adducts described in 4.3.2 and 4.3.3 as ligands to prepare $Ru(bpy)_n$-C_{60} dyads **51-54**, scheme 17, both solubility and reactivity obstacles had to be overcome. The fullerene derivatives used in this work are not very polar, and thus not soluble in ethanol. $Ru(bpy)_2Cl_2$, **1**, on the other hand is not soluble in non-polar solvents. Another question was the possibility of obtaining complexes **53** and **54**, or whether the ligands **49** and **50** would be to sterically hindered to allow coordination.

Complexes **51**, **52** and **53** was prepared by refluxing the corresponding ligands **42**, **47** and **49** together with **1** in a mixture of equal amounts toluene

and ethanol, and the products precipitated upon addition of NH_4PF_6. The solvent mixture ensured sufficient solubility of both the fullerene containing ligand and **1**. UV-vis spectra for the obtained complexes show features characteristic for ruthenium bipyridine complexes, such as broad absorption bands between 400 and 500 nm. However, the formation of **51**, **52** and **53** can be subjected to further improvements.

In the preparation of **53**, some different solvents were evaluated the toluene-ethanol mixture. 2-Methoxyethanol has, in this context, the advantage over ethanol by being slightly less polar. It has also a higher boiling point (125 ºC) which can promote the reaction, but when using toluene and 2-methoxyethanol (1:1) no reaction could be detected. THF had the ability of dissolving both ruthenium salt **1** and ligand **49**, but nor in this case did any reaction occur. Carbon disulphide is a good solvent for fullerene derivatives. Performing the reaction in carbon disulphide and ethanol (1:1) resulted in a precipitate when adding NH_4PF_6, but the product was not stable and decomposed within minutes. As fullerene ligand **50** contains two nitro groups and should be more polar than analogue **49**, one attempt to obtain complex **54** was carried out in 2-methoxyethanol instead of using a mixture of ethanol and toluene. However, no reaction occurred.
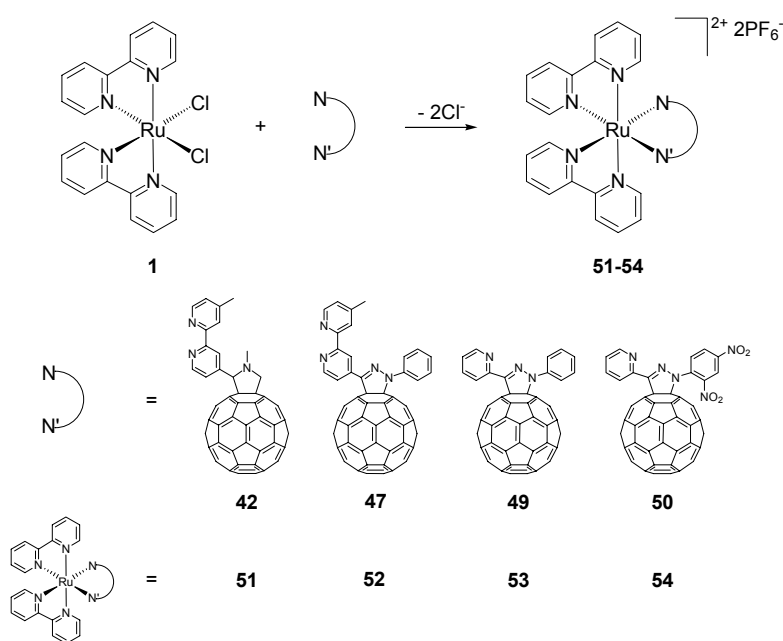
Scheme 17. An overview of dyad-formation reactions.

By addition of a silver salt to the reaction mixture, the ability of the metal in $Ru(bpy)_2Cl_2$ to coordinate further neutral ligands is increased, as Ag^+ reacts with the chloride ions and precipitates as AgCl. Upon adding $AgBF_4$ to reaction mixtures containing ligands **42** and **47**, the formation of complexes **52** and **53** proceeded very smoothly. However, when heading towards **51**, the presence of $AgBF_4$ resulted in a solid with very low solubility in common solvents (dichloromethane, diethyl ether, ethyl acetate, acetonitrile etc.). Some attempts were also made using $AgPF_6$ instead of $AgBF_4$ and NH_4PF_6 in the preparation of **53** and **54** which resulted in products with a high solubility in water.

The reasons for these different behaviours have not yet been elucidated. Simple control experiments where $AgBF_4$ and $AgPF_6$ was added to solutions of ligands **42**, **47** and **49**, resulted in colour changes of the ligand solutions followed by formation of precipitates. Identification of these products is in progress. A possible explanation for these observations is coordination of the silver ion to any of the amines present in the ligands.

A conclusion from this work is that it is possible to obtain this type of $Ru(bpy)_n$-C_{60} dyads, even the tight complex **53**. Still, the reactions have to be studied further in order to get an understanding on how the silver salts affects the product formation and how to improve the yields.

4.3.5   Reactions on coordinated bipyridines

In chapter 4.1 two routes to $Ru(bpy)_n$-C_{60} dyads were presented, differing in at what step the C_{60}-unit is introduced. Either the fullerene was substituted with a bipyridine ligand followed by coordination to the metal or the complex is formed before the addition to the C_{60}. As aldehydes are used in the preparation of the fullerene adducts **51-54** described in the previous chapter, the focus in the alternative approach was to perform reactions on complex **55**. This $Ru(bpy)_2bpy$–aldehyde complex can be obtained in good yields by refluxing **1** and **40** in ethanol, scheme 18.

As the synthesis of the azomethine ylides and nitrile imines required for cycloadditions to C_{60} involves nucleophilic attack of a nitrogen atom on the aldehyde carbonyl carbon, an initial survey of reactions of this kind was carried out to get an idea of the behaviour of the aldehyde group in **55** compared to that of **40**, scheme 18.

36
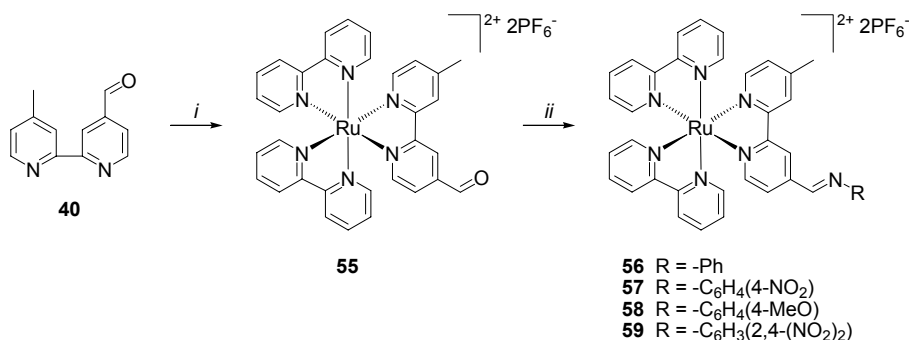
Reagents and conditions: i) Ru(bpy)$_2$Cl$_2$, EtOH, reflux, 15 h, then NH$_4$PF$_6$ (73 %); ii) RNH$_2$, EtOH or CH$_2$Cl$_2$

Scheme 18. Reactions of **55** towards imine derivatives

It turned out that the outcome of these reactions were more affected by the choice of solvent than of the different amines used.[92] When the reaction was carried out in dichloromethane almost quantitative yields were obtained, whereas almost no reaction at all occurred in ethanol. This is probably due to the low solubility of the complex **55** in ethanol.

Attempts were made to obtain the dyad **51** by treating the complex **55** with C$_{60}$ and *N*-methylglycine in toluene, scheme 19. However, only a very small amount of product was formed. The ^{1}H NMR spectrum of crude **51** showed the three pyrrolidine protons with very distinctive signals as one singlet and two doublets at 4-5 ppm, an area with few other signals. However, the integrals of these signals relative to the other signals present indicated that the sample contained too little product to isolate. As toluene is not an optimal solvent for complexes like **55**, this reaction would be possible to improve by changing solvent.
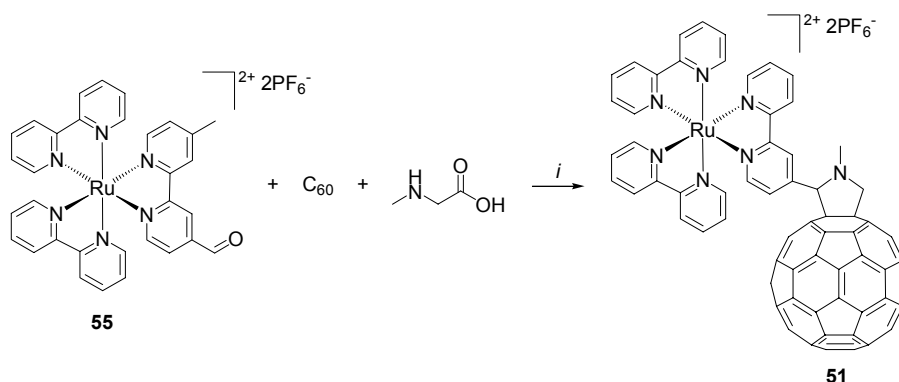
Reagents and conditions: i) toluene, reflux, no product isolated.

Scheme 19. Formation of fulleropyrrolidine starting from aldehyde complex **55**.

4.4 Characterisation of adducts

4.4.1 Methanofullerenes in solar cells

In 1997, Kamat *et al.* reported that C_{60} could inject electrons into TiO_2.[93] They also state, however, that C_{60} adsorbs poorly on TiO_2. We wanted to elucidate whether the electron-injecting capacity is changed if the C_{60} is bound to the TiO_2. Therefore, simple solar cells containing TiO_2-electrodes treated with the fulleromalonic acid **26** were prepared, figure 10. These electrodes were prepared in the same manner as described in chapter 3.1.3. In addition, electrodes treated with **25** were studied.
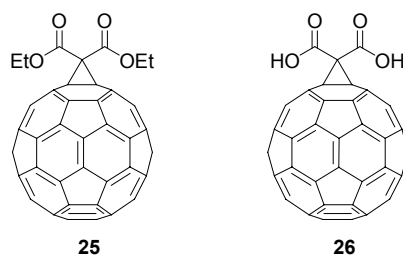

Figure 10. Methanofullerenes evaluated in solar cells.

IPCE-measurements, figure 11 showed that the current obtained with the fullerene-treated electrodes was lower than when using bare TiO_2-electrodes. There were no obvious differences between electrodes treated with **25** or **26**, or with different sensitising times.
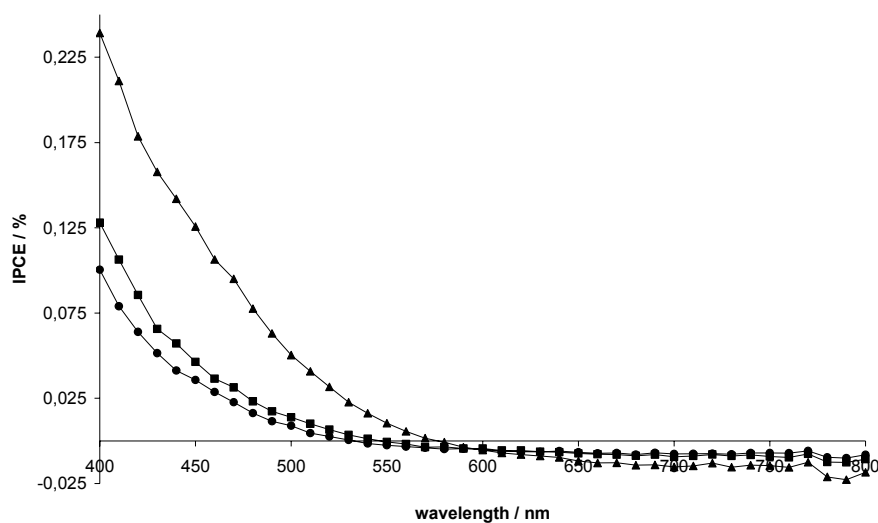
Figure 11. IPCE-curves for bare TiO_2-electrodes (▲), electrodes treated with **25** (●) and **26** (■).

The appearance of the IPCE-curves can be explained by looking at the redox potentials for the components used, figure 12. The potential for the conduction band and the valence band in TiO_2 is -0.5 V and +2.5 V respectively. The first reduction potential of C_{60} is between approximately -0.3 V and -0.7 V depending on solvent, electrolyte and temperature. Similar values have been reported for functionalised C_{60} in which also the substituents influences the potential[94] (all potentials given *vs.* NHE). C_{60} is not readily oxidised and its oxidation potentials are reported to be around +1.5 and +2.0 V.[94] The exited fullerene can be oxidised more easily with potentials around 0 V [93]
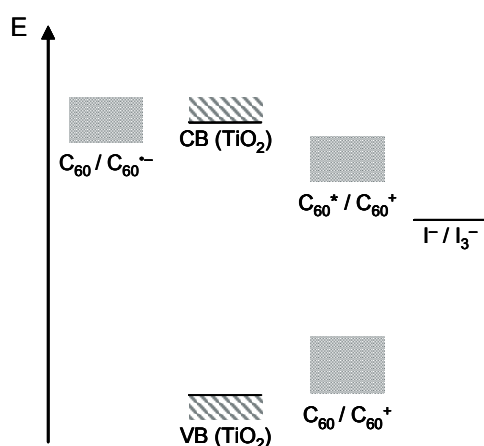

Figure 12. A schematic overview of some redox potentials for TiO_2, C_{60} and I^-/I_3^-.

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As the reduction potentials for the fullerenes, the oxidation potentials for excited C_{60} and the conduction band of TiO_2 are very close to each other, there is the possibility to get either electron injection from excited fullerene into TiO_2, or reduction of the fullerene by the photoexcited oxide electrons in the conduction band. If the latter process is occurring in the studied solar cells, electrons would move from the semiconductor to the fullerene instead of to the back contact. Such a reaction would result in a lowering of the IPCE for the treated electrodes compared with the non-treated ones. Another explanation for the decrease in IPCE would be that the fullerene coating blocks the light from reaching the TiO_2. Irrespective of the reason of the decrease in IPCE when using **25** or **26**, the results shows that they are no good for use as dyes in this kind of solar cell.

A different approach to use fullerenes in dye-sensitised solar cells is by not attaching the fullerene directly on the surface of the semiconducting metal oxide, as with the fulleromalonates, but to use a $Ru(bpy)_n$-C_{60} dyad that can be connected to the semiconductor *via* the bipyridines. This is a work in progress regarding the preparation of analogues of **51-54** where the bipyridines are replaced by 4,4′-dicarboxy-2,2′-bipyridines. A similar approach has been reported, but then pristine C_{60} was deposited onto the dye coated TiO_2 and not covalently bound to the dye.[95] That study concluded that the presence of the fullerene protected the dye from degradation induced by the electrolyte

4.4.2 Spectroscopic evaluation of dyads

To get a better understanding of the photoelectrochemical properties of the $Ru(bpy)_n$-C_{60} dyads **51-54**, spectroscopic and photophysical measurements are planned to be carried out. To be able to evaluate the results, complexes **60** and **61** were prepared to be used as references, resembling the complexes in the dyads without the fullerene moiety, figure 13. Complexes **60** and **61** were obtained by refluxing the hydrazone ligands and $Ru(bpy)_2Cl_2$ in ethanol followed by addition of NH_4PF_6.
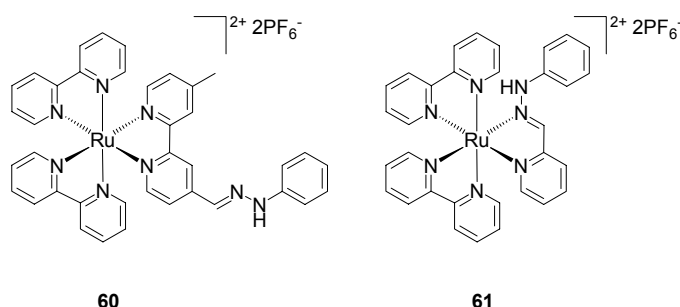

Figure 13. Hydrazone based complexes prepared.

Preliminary results from emission studies[§] shows that **60** and **61** are not ideal as references because **60** has a very low emission and **61** did not give any emission at all, figure 14. Complexes similar to **61** have earlier been reported to show emission.[96] The complex moiety in **51** and **52** are fairly similar to $Ru(bpy)_3$ and their emission spectras can thus be compared. $Ru(bpy)_3$ shows a large emission around 610 nm whereas **51** does not emit in that area. This means that the excited state of the complex is completely quenched. To elucidate whether this is due to electron- or energy transfer further studies have to be carried out. For **52** and **53** which show some emission, the degree of quenching is rather large when compared to $Ru(bpy)_3$. The present emission for **52** and **53** might be a result of the hydrazone moieties as they are chromophores in themselves.

[§] made by Prof Leif Hammarström, Department of Physical Chemistry, Uppsala University
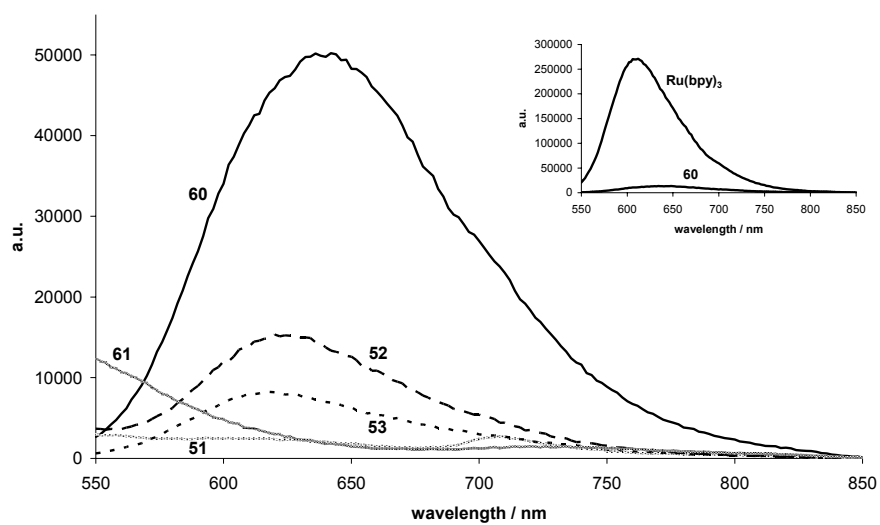
Figure 14. Emission spectra for complexes **51**-**53** and **60**-**61** using 4 mm slits. The inset shows the emission spectra for Ru(bpy)$_3$ and **60** using 2 mm slits.

5 Summary and outlook

In this thesis the work of preparing new photoactive substances has been presented together with initial evaluations of their photoelectrochemical and photophysical properties.

- $Ru(bpy)_2(4\text{-thiopyridine})_2 \cdot 2PF_6$ was prepared and used in Grätzel type solar cells based on ZnO. The results show that the complex is able to inject electrons into the oxide surface.

- Several different routes were tried out to prepare $Ru(bpy)_2(4,4'\text{-dithio-}2,2'\text{-bipyridine})_2 \cdot 2PF_6$ in order to elucidate whether this complex would give higher efficiencies than the pyridine analogue when used in solar cells. Due to reactivity difficulties, this project was later put on hold.

- Several fullerene C_{60} derivatives have been synthesised based on methanofullerenes, fulleropyrrolidines and –pyrazolines.

- The use of fullerene substituted malonic acid and its ethyl ester as dyes in solar cells resulted in even lower efficiencies (IPCE) than for bare TiO_2. Due to the low reduction potential of fullerenes, the electron probably moves from the TiO_2 to the fullerene instead of to the outer circuit.

- Three $Ru(bpy)_n$-C_{60} dyads with short linkers between the electron donating and –accepting moieties have been prepared. Their syntheses proved to be highly sensitive to the choice of solvent and to the presence of different solver salts like $AgBF_4$ and $AgPF_6$. These reactions have to be studied further to improve the outcome of the reactions.

- A preliminary evaluation of the emission of the three dyads showed almost complete quenching of the excited sate of the pyrrolidine-based dyad, whereas there was some remaining emission from the pyrazoline-based ones. Whether this was due to incomplete quenching of the excited states or induced by the presence of hydrazones is an interesting question and remains to be revealed.

6   Summary in Swedish

Syntes och utvärdering av fotoaktiva pyridinkomplex för elektronöverföringsstudier och fotoelektrokemiska tillämpningar

I den här avhandlingen diskuteras synteser av olika molekyler som har det gemensamt att de innehåller bipyridinenheter som koordinerats till rutenium. Sådana komplex kan också absorbera ljus och somliga har därigenom förmågan att överföra elektroner till antingen en metalloxidyta eller en fullerenenhet, figur I. Förhoppningen är att studier av dessa molekyler skall kunna bidra till bättre förståelse och utveckling av metoder att ta till vara solenergi, till exempel solceller.
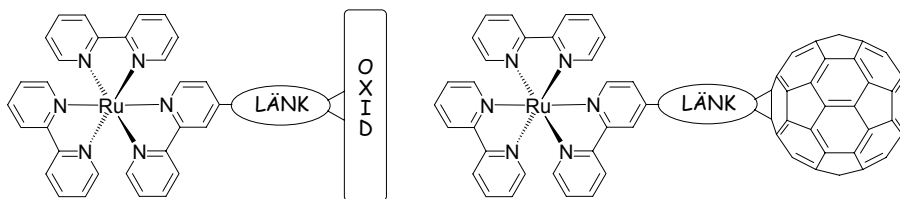

Figur I. Schematisk bild av rutenium-bipyridinkomplex bundna till en metalloxidyta eller en fullerenenhet.

Det används väldigt mycket energi i dagens samhälle och efterfrågan ökar ständigt. Den mesta av energin kommer från fossila bränslen såsom olja, kol och naturgas. Då dessa är icke-förnyelsebara med begränsad tillgång gör den stora förbrukningen att resevoarerna töms i snabb takt. Inom en tämligen snar framtid kommer det därför att krävas andra sätt att producera energi i tillräcklig mängd. Den kanske mest intressanta källan som i mänsklighetens tidsperspektiv är oändligt tillgänglig och oändligt rik är solen. Energin från solen som varje dag träffar jorden är tillräckligt stor att om vi kunde ta hand om den i större utsträckning än vad som sker idag, skulle många energiproblem kunna lösas.

Det finns olika sätt att ta hand om solens energi av vilka solceller är det vanligaste. I dessa omvandlas solljuset till elektricitet. Ett annat sätt är s.k. solfångare där energin används för att värma vatten. Detta kan i sin tur an-

vändas direkt för att värma till exempel hus, eller till turbiner för att generera el. Dessa två varianter finns kommersiellt tillgängliga redan nu. För att de skall kunna ersätta fossila bränslen måste de dock bli mer effektiva och framför allt billigare så att metoderna används i betydligt högre grad än vad som sker idag. Ett tredje sätt att ta tillvara på solens energi, som dock bara är på forskningsstadiet, är vad som kallas artificiell fotosyntes. Detta går ut på att härma växternas fotosyntes; solenergin används för att driva kemiska reaktioner och bilda energirika produkter. I den naturliga fotosyntesen ombildas koldioxid till tex kolhydrater och proteiner. Tanken med artificiell fotosyntes är att använda solenergin till att omvandla vatten till bland annat vätgas som sedan kan användas som ett väldigt rent bränsle då den enda förbränningsprodukten är vatten.

Det finns ett flertal olika typer av solceller där den vanligaste är baserad på kiselkristaller. En nackdel med dessa är att de är dyra då det krävs hög kvalitet på kristallerna. Grätzelceller kallas en annan typ av solceller, som har fördelen att de kan göras väldigt billiga för konsumenten. De består av flera komponenter, bland annat av en yta som belagts med små partiklar av titandioxid. Dessa partiklar kan inte själva ta upp synligt ljus och måste därför täckas med ett färgämne. Detta absorberar ljuset och överför energin till en elektron som finns i färgämnesmolekylen. Elektronen får då i sin tur tillräckligt med energi för att kunna hoppa över till oxiden och därifrån transporteras iväg för att användas som elektricitet. Färgämnet är oftast ett ruteniumbipyridinkomplex ($Ru(bpy)_n$) och för att färgämnet skall sitta kvar på oxidytan behövs det länkgrupper på bipyridinerna vilka har till uppgift att binda till oxidytan. I nuläget är det mest karboxylsyror som används som länkgrupper, men för att kunna förbättra Grätzelcellerna kan det vara nödvändigt att hitta andra länkar mellan halvledaren och färgämnet. Till exempel har det konstaterats att om zinkoxid används istället för titandioxid så uppstår problem med att färgämnet inte sitter fast ordentligt. I den här avhandlingen diskuteras syntesen av ett komplex innehållande tioler, grupper som innehåller svavel, som skulle kunna fungera som länk till zinkoxid, figur II.
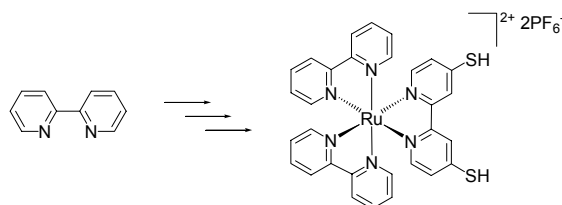
Figur II. Ett tiolsubstituerat ruteniumkomplex kan tillverkas i flera steg utgående från 2,2´-bipyridin.

Utgående från 2,2´-bipyridin tillverkades 4,4´-diklor-2,2´-bipyridin i tre steg, vilken i sin tur användes i försök att introducera tioler på pyridinringarna. Trots flera olika tillvägagångssätt har dock inte det önskade komplexet kunnat isoleras. Studier av ett snarlikt komplex har visat att tiolerna binder till zinkoxidytan och hjälper till att överföra elektroner. Det är därför motiverat att fortsätta arbetet med att framställa svavelinnehållande färgämnen för utvärdering i solceller av Grätzeltyp.

En annan del av den här avhandlingen behandlar syntesen av olika dyader, figur III. Detta är molekyler som består av två olika delar, en del som kan ge ifrån sig elektroner och en som kan ta emot elektroner. Den elektrondonerande delen är ruteniumkomplex av samma typ som används till solcellerna ovan. Den elektronaccepterande delen har i det här arbetet varit fullerener som är en form av rent kol. De fullerener som använts här är av den minsta sorten och består av 60 kolatomer (C_{60}). Det som är speciellt med fullerener är att de är väldigt bra på att ta emot och behålla elektroner, upp till sex stycken samtidigt. Detta är en egenskap som skulle kunna användas i till exempel artificiell fotosyntes där den elektrondonerande delen av dyader skall absorbera ljus, exempelvis från solen, för att kunna föra över en elektron till elektronacceptorn. De uppsamlade elektronerna skall sedan kunna användas för att driva kemiska reaktioner. Principen är alltså densamma som för solceller med skillnaden att elektronerna används på olika sätt.
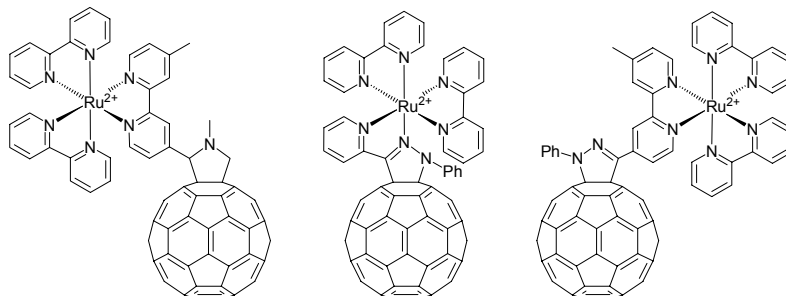
Figur III. Tre Ru(bpy)$_n$-C$_{60}$ dyader för vilka synteserna beskrivs i avhandlingen.

På samma sätt som i solcellerna måste det finnas något som binder komplexet till fullerenen. I det här arbetet har synteser av olika varianter på dyader mellan rutenium-bipyridinkomplex och C_{60} diskuterats. Skillnaden mellan dyaderna har i huvudsak varit sättet på vilket komplexet fästs vid fullerenen. Längden och utseendet på länken påverkar bland annat hastigheten med vilken elektronerna överförs men skall även motverka att elektronen hoppar tillbaka till utgångsläget. Oftast används relativt långa länkar för detta ända-

mål, men med dyaderna som presenteras i den här avhandligen har tanken varit att använda så korta länkar som möjligt.

I arbetet med att hitta framkomliga vägar för att tillverka de önskade dyaderna har frågor rörande löslighet och reaktivitet hos de olika föreningarna uppkommit och diskuterats. I synnerhet har försök med tillsatser av silversalt till reaktionsblandningarna visat sig ge oväntade resultat. Detta är något som kommer att kräva mer arbete för att utreda. Mätningar skall göras som kan visa hur de korta länkarna påverkar elektronöverföringen från ruteniumkomplexet och fullerenen jämfört med de strukturer som sedan tidigare presenterats. Preliminära studier av några dyader visar att det troligen förekommer elektronöverföring från komplexdelen till fullerenen men att det behövs ytterligare undersökningar för att klargöra mer i detalj vad som sker i dyaderna vid belysning.

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